EFFECT OF CATALYSTS ON THE DEFLAGRATION RATE OF AMMONIUM PERCHLORATE

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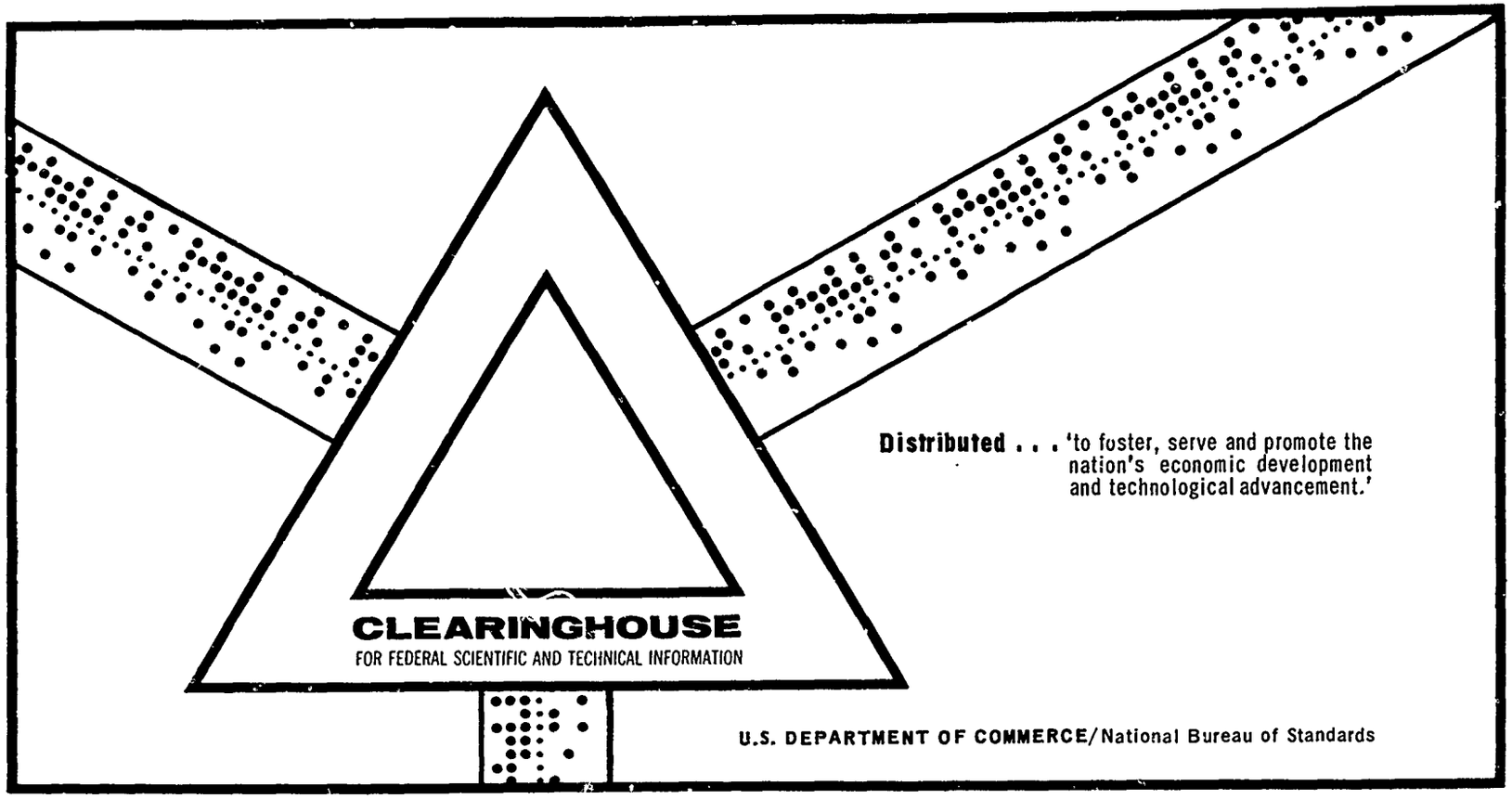
30 June 1969



AFOSR SCIENTIFIC REPORT

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PRINCIPAL INVESTIGATOR: E. E. PETERSEN

PREPARED FOR
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ABSTRACT

One objective of the work during this period was to find the effect of catalytically active impurities on the deflagration rate of ammonium perchlorate. In the present study the burning rates of polycrystalline pellets of ammonium perchlorate from three sources and with different degrees of recrystallization[2] were measured and compared. The burning rate changed considerably in the first three successive recrystallizations and the data showed that the impurities affected the burning rate especially at high pressures. It was also found that occluded water in ammonium perchlorate pellets changed the deflagration rate considerably. These results indicate that one of the reasons for the disagreement among different investigators on the burning rate of ammonium perchlorate might well be the effect of traces of residual impurities which existed in the crystals and pellets used in the studies even after purification by recrystallization. The present study also indicates that the nature of impurities in the "as received" or recrystallized ammonium perchlorate depends on the source of supply.

It was also found that pressing uniform pellets of reproducible quality is very difficult. This is believed to be another possible source of scatter in the existing data.

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[2] "Degree of recrystallization" is used hereinafter to mean the number of times ammonium perchlorate is successively recrystallized.

To improve the pelletizing process, a vacuum floating-type die was designed.

Considerable experimental evidence exists which indicates that the distribution of catalyst, whether isomorphically substituted into the crystal lattice or mechanically mixed with propellants prior to pressing, has relatively little effect on its performance. To understand better the important parameters needed to explain the experimental data, a theoretical study was carried out.

A mathematical model was developed to calculate the effectiveness factor for surface reactions coupled with surface diffusion on a solid-catalyst surface or bulk diffusion near the burning surface, with discrete adsorption centers. The solutions for integral-order reactions are presented. The combined effect of intrinsic reaction and surface diffusion results in apparent orders of $\frac{n+1}{2}$ and apparent activated energies which are the arithmetic average of those for surface diffusion and chemical reaction. A useful approximate solution has been obtained to give a closed-form solution to the second-order reaction case for the proposed model. Order-of-magnitude calculations using these results indicate that surface or bulk diffusion may be fast enough so that even with mechanical mixtures of $KMnO_4$ in NH_4ClO_4 the effectiveness factor is essentially unity in corroboration with experimental findings.

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CHAPTER I

INTRODUCTION

Composite propellants have a large-scale application in the propulsion of many space-age vehicles. They are generally formed by embedding a finely divided oxidizer in a plastic or resinous fuel matrix. Various catalysts, plasticizers or binders are also added in small quantities. The most commonly used oxidizer is ammonium perchlorate, NH_4ClO_4.

Composite propellants are complex heterogeneous systems, and very little is known about the chemical details of their combustion. Many investigators have studied the combustion of pure ammonium perchlorate, which is believed to be less complex yet very important in giving an insight into the nature of the composite systems.

Ammonium perchlorate undergoes deflagration (combustion characterized by a self-sustained flame which propagates with a velocity lower than the speed of sound) provided the ambient pressure is above its deflagration limit. There is an extensive literature in this field. Pittman (14), Friedman (10,11), Engleman (9) and Watt (22) have reviewed these investigations. Most of the studies on the ignition and deflagration of ammonium perchlorate made use of either polycrystalline cylindrical pellets or single crystals. The deflagration of polycrystalline pellets is more complicated than that of single crystals, probably owing to multiple ignition phenomena (16,17,18).

One of the important studies on ammonium perchlorate is the determination of its steady-state deflagration rate. This has been the subject of much research (5,6,9,10,13,16, 22). Despite this extensive research there has not been good agreement among the rates reported. For example, there has been some disagreement about the change in the burning rate of single crystals with pressure changes in the range 500-5000 psia. Hightower and Boggs (6) reported that the burning rate at room temperature increased with pressure up to a maximum of 1.2 cm/sec around 2000 psia and then sharply decreased with further increase in pressure up to 4000 psia. Similar experiments by Watt (22) showed that the rate increased to a maximum of about 1.1 cm/sec at 700 psia, and after passing through a minimum around 1000 psia increased with further increase in pressure. In order to test whether differences in apparatus were the source of this disagreement, the two research groups exchanged the crystals which each had grown. Although they observed a slight effect of apparatus on the burning rate, the two different isotherms previously reported were nearly reproduced again. This was an indication that the major source of the disagreement was some intrinsic difference in the crystals rather than in the apparatus. Figs. I-1a and 1b show a comparison between some of the existing data on the burning rate of ammonium perchlorate. As shown, the burning rates reported vary from 0.63 to 1.1 for 1000 psia ambient pressure and from 0.3 to 1.2 for 3500 psia. However, these differences cannot be readily attributed to particle

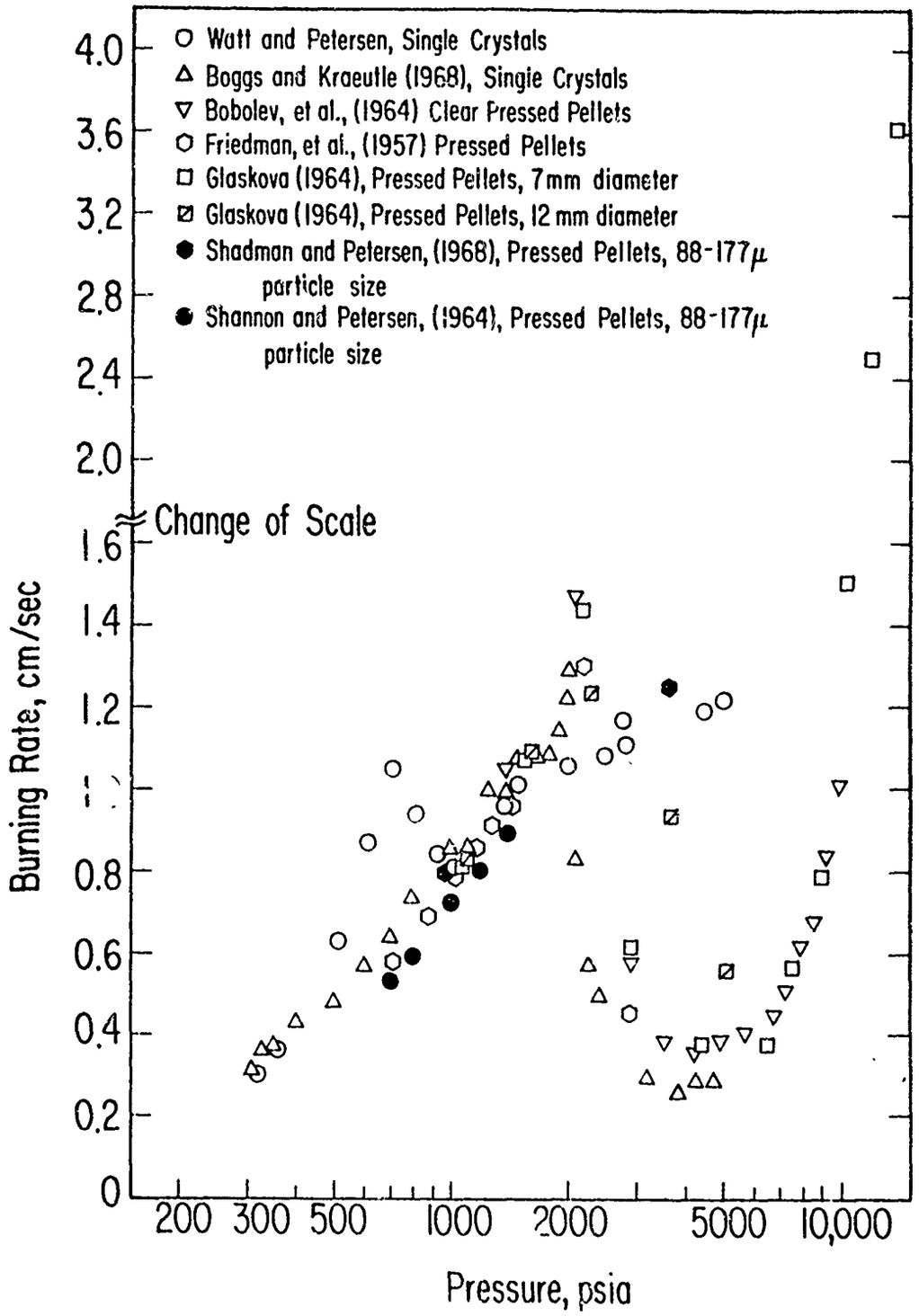


Fig. I-1a. Comparison of room temperature burning rates of AP single crystals and pressed pellets. [Data of Watt (22)]

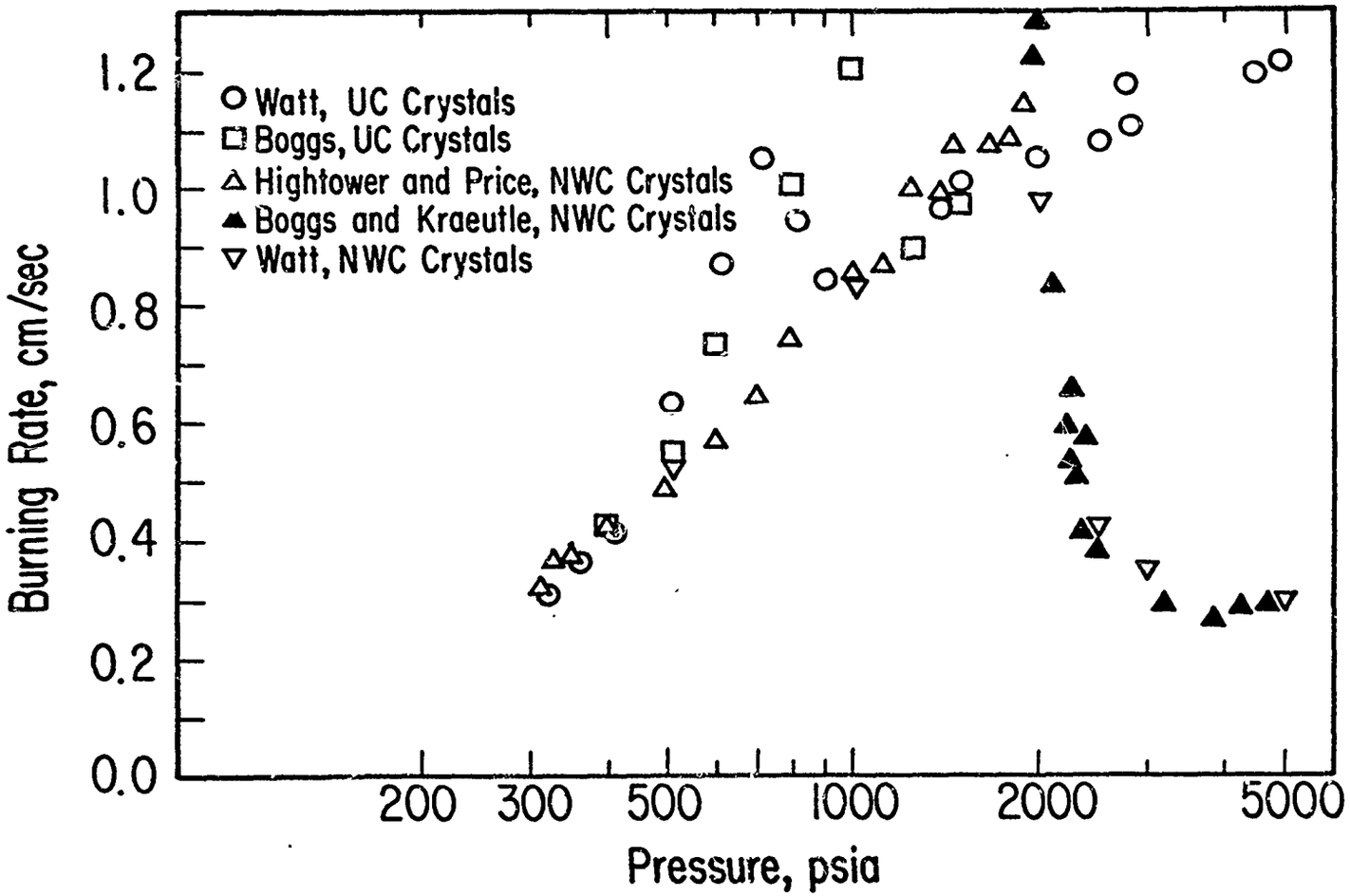


Fig. I-1b. Comparison of room temperature burning rates of AP single crystals grown at U.C. and at NWC. [Data of Watt (22)]

size effects nor to variations in apparatus and measuring methods.

There has been some evidence that the burning rate is very sensitive to some impurities which exist in ammonium perchlorate, even though present in very small amounts. Adams et al. (1) compared the burning rate of ammonium perchlorate from two sources of supply and found that the burning rate of "as received" material at 1000 psi was 1.2 cm/sec for the sample from source "A" and 0.7 cm/sec for that from source "B". Once-recrystallized ammonium perchlorate from both sources burned at 0.67 cm/sec. It was found that "as received" "B" contained 125 ppm lead. So these workers reported that there was an unidentified positive catalyst in the "as received" samples of "A" and "B" which was suppressed in sample "B" by the negative catalytic effect of the lead compound. They did not make any further analysis of the effect of recrystallization. Engleman (9) also found that "as received" reagent-grade ammonium perchlorate burned at 1.08 cm/sec at 1000 psi, while a similar pellet made from the ground crystals of ammonium perchlorate from the same source burned at 0.84 cm/sec.

Many investigators have used "as received" reagent-grade ammonium perchlorate and have presumed that the traces of impurities do not affect the burning rate considerably. Most of the others have assumed that one or two recrystallizations are enough and further purification is not necessary (3,4,7,12,20). Bircumshaw and Newman (3,4) reported that

the rate of decomposition of twice-crystallized and that of seven times recrystallized ammonium perchlorate were the same and they concluded that two successive recrystallizations were enough in that study. However, it is not known whether the effect of impurities on the decomposition rate is the same as on the deflagration rate.

Smith (19) measured the burning rate of ammonium perchlorate from three sources and with different degrees of recrystallization. In this study he burned polycrystalline pellets of ammonium perchlorate at room temperature and under 1000 psi ambient pressure. He found that, for ammonium perchlorate from one supplier, the rate increased by successive recrystallizations and then levelled off to a limit of 0.75 cm/sec. For the other two, the scatter of experimental data was so extensive that no definite conclusion could be drawn regarding the trend of the change. However, there was an indication, as he reported, that the rates increased to a maximum and then decreased with further recrystallization. He made a spectrochemical analysis of the samples for some metallic impurities, but the results did not show anything that could explain this change in burning rate. He also reported that some pellets extinguished before complete burning and usually left some tiny black particles on the extinguished surface. Some apparent differences in the optical properties of the pressed pellets were also observed.

In addition to the above studies, there has been some investigation on the effect of known catalysts added to

ammonium perchlorate. Friedman et al. (10) studied the effect of $CuCrO_4$, CuO, Fe_2O_3, Cr_2O_3, $NaMnO_4$, MnO_2, CaO and $CaCO_3$ on the deflagration of ammonium perchlorate. They found that these catalysts increased the burning rate at high pressures considerably. The following table shows this increase at 3700 psia and with 3 percent catalyst content:

Catalyst	Burning rate of AP with catalyst/ Burning rate of pure AP
$CuCrO_4$	25
CuO	14
Fe_2O_3	9
MnO_2	6

However, there has not been enough study in this field and very little is known about the nature and extent of the catalytic effect on the deflagration.

In view of the background just outlined it seemed necessary to make a careful study of the effect of natural impurities and added catalysts on the deflagration of ammonium perchlorate. The study of the effect of natural impurities was necessary for two major reasons: First, it was important in detecting the nature of catalysts and inhibitors which exist in ammonium perchlorate from different sources. Second, it could show whether impurities were the major source of scatter in the existing data. Therefore such a study, described in Chapter II, was the first objective of the present work.

In most recent investigations on the deflagration of

ammonium perchlorate, single crystals have been preferred to pressed pellets because the single crystals burn more uniformly and their deflagration is not influenced by possible complex intercrystalline effects. They are also preferred in the study of the effect of catalysts which are isomorphic with ammonium perchlorate, because it is possible to grow single crystals in which the catalyst is dispersed uniformly at the atomic level.

CHAPTER II

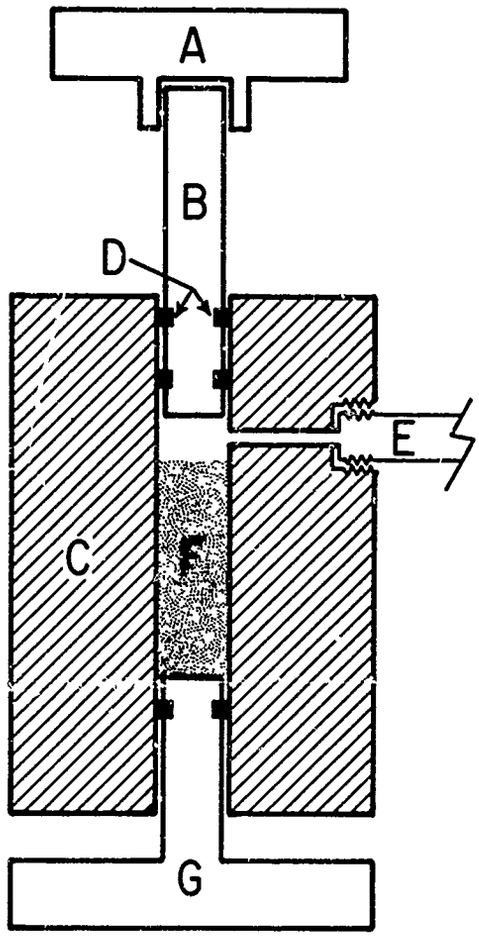
EFFECT OF SUCCESSIVE RECRYSTALLIZATIONS ON THE DEFLAGRATION RATE OF AMMONIUM PERCHLORATE

Introduction

Ammonium perchlorate is usually purified by successive recrystallizations. Although most investigators have used recrystallized ammonium perchlorate in combustion studies, little work has been done to evaluate the effectiveness of the method in obtaining samples of high enough purity for the study of the intrinsic deflagration properties of ammonium perchlorate. Therefore, as a first step in the study of impurities, the effect of recrystallization on the burning rate of polycrystalline pellets of ammonium perchlorate was investigated. Since samples from different sources with different degrees of recrystallization had to be studied, pressed pellets were used instead of single crystals because of the difficulties and length of time involved in growing single crystals from each sample.

Experimental Apparatus

Pelletizing Apparatus. - A cylindrical vacuum die was designed and made from E9310 carburized steel. A schematic diagram of the die is shown in Fig. II-1. This die was the floating type and therefore could provide a better distribution of the pelletizing pressure than a die having a fixed plunger. It was designed for the maximum safe pelletizing pressure of 150,000 psi. Pellets pressed in this die had a



A = Cap for the upper plunger
B = Upper plunger
C = Die body
D = O-rings
E = Vacuum tube
F = AP powder
G = Lower plunger (base)

Fig. II-1. Schematic diagram of pelletizing die.

diameter of 3/8 in. and length of 0.5 - 1 in. Air between the powder particles could be pumped out through a vacuum tube. Three O-rings, placed in the special slots of the upper and lower plungers, provided seals. Two O-rings were used on the upper ram in order to hold the vacuum by one of them as the other was passing the vacuum hole. A minimum pressure of about 50 microns could be maintained by this set-up. An Elmer Engineering 30-ton laboratory hydraulic press (Elmer Engineering, Detroit, Mich.) was used for pressing the pellets.

Combustion System. - A schematic diagram of the combustion system is shown in Fig. II-2. The apparatus consists of three major parts: combustion chamber, photographic system, and control center. Figures II-3 and II-4 show the first two. A brief description of these parts follows; Watt (22) has described this apparatus in detail.

(a) Combustion Chamber: The combustion chamber is a stainless-steel cylinder. Both ends of this cylinder are threaded and are fitted with stainless-steel end plates, O-rings and threaded aluminum compression caps. Two quartz windows, mounted in two cylinders perpendicular to the chamber, are provided for photographing the pellets during combustion. The combustion chamber is mounted on a support fastened to the base of a safety shield. Cylinders of nitrogen are used for pressurizing up to 5000 psi. To minimize the pressure fluctuations during the combustion, an auxiliary stainless-steel

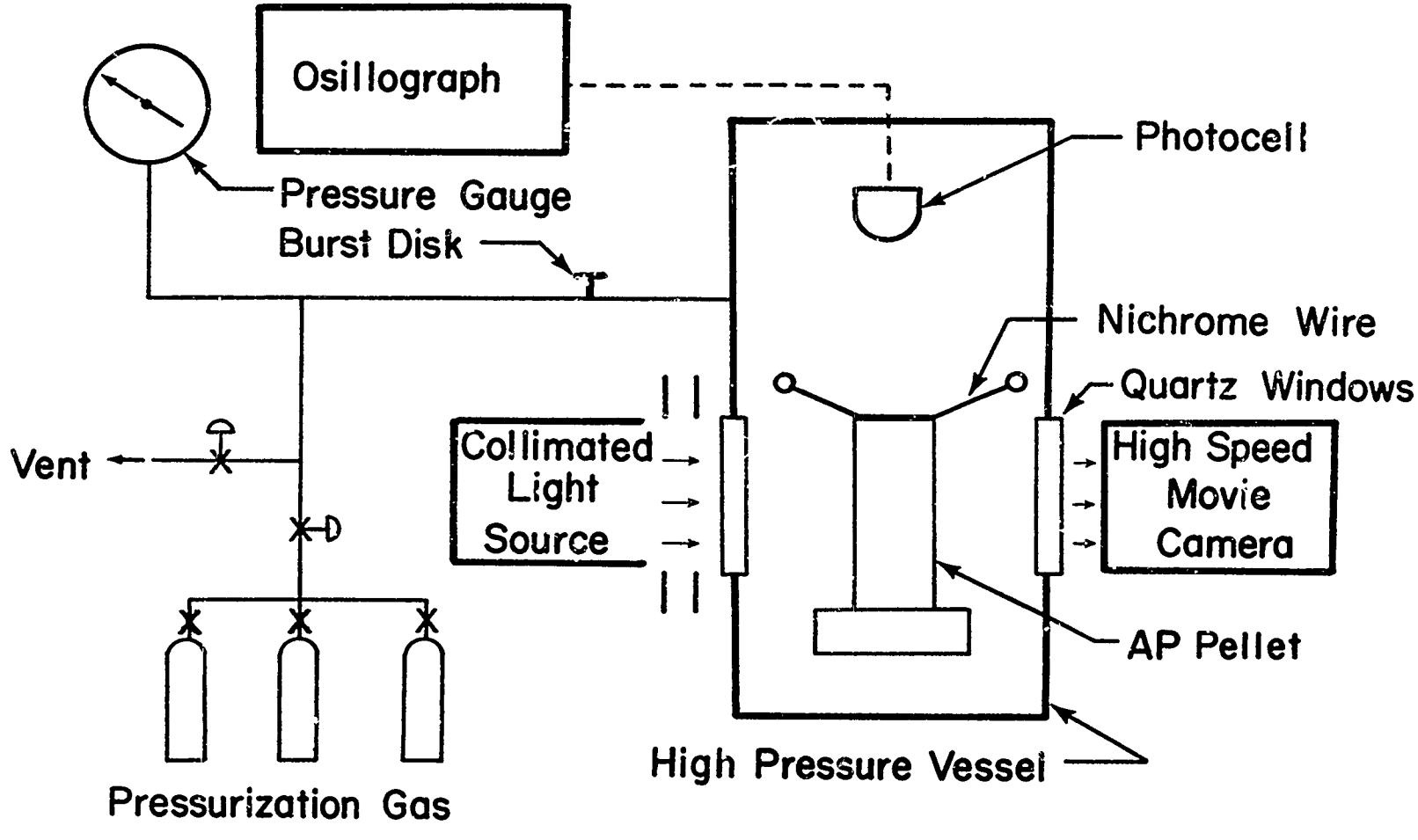


Fig. II-2. Schematic diagram of combustion apparatus.

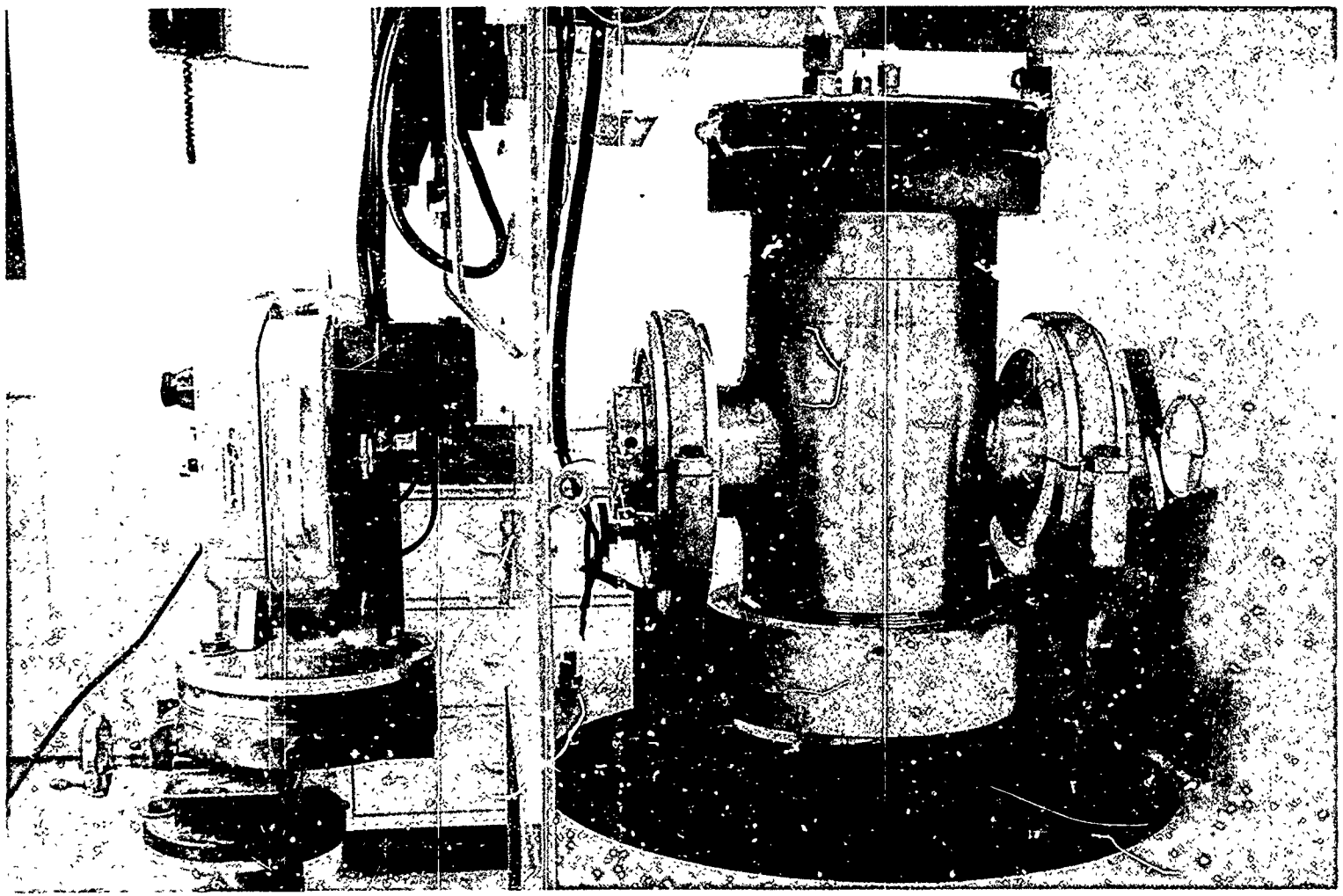


Figure II-3. Combustion chamber and high speed movie camera.

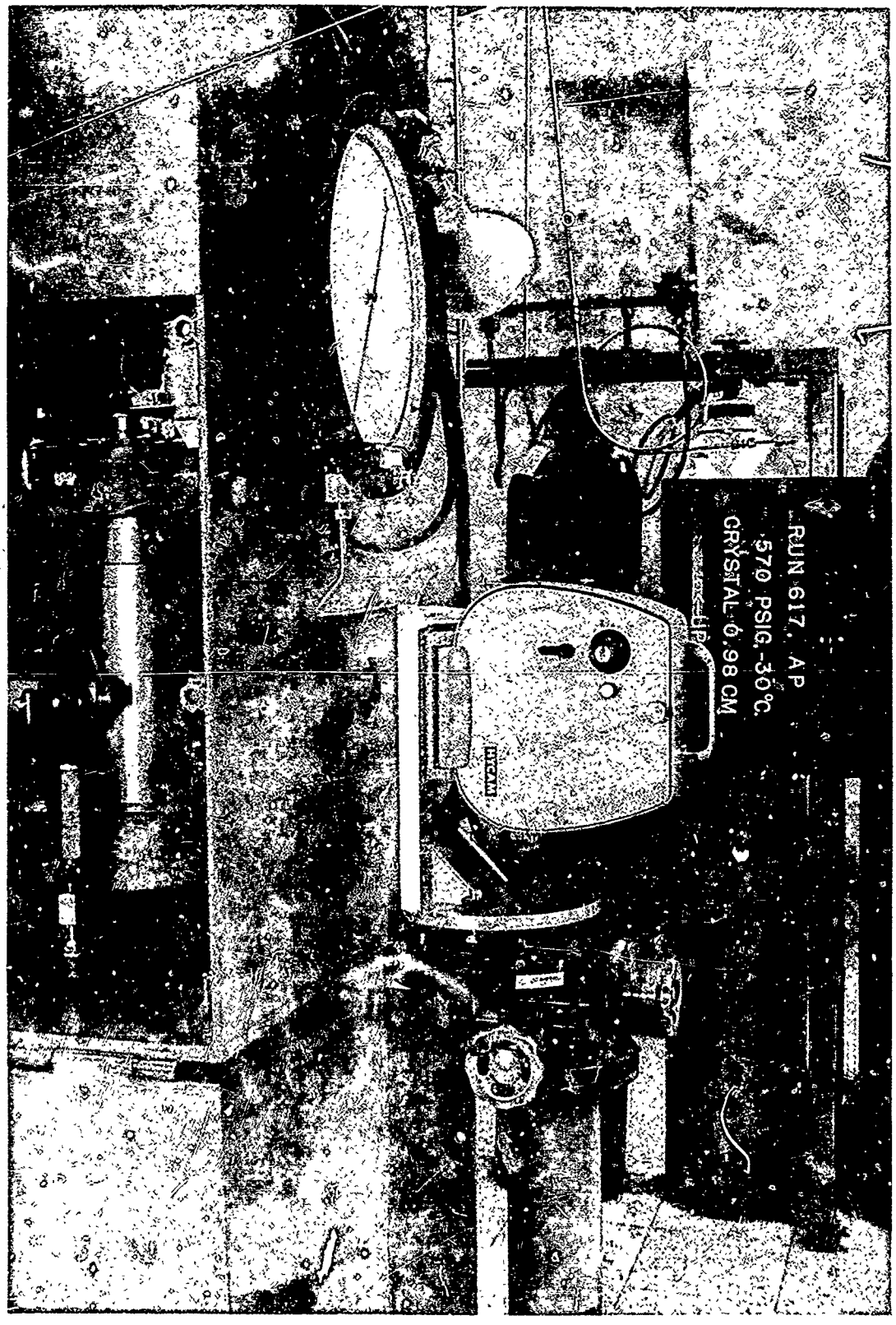


Figure II-4. Combustion chamber, high speed movie camera, and titling board.

surge tank is attached to the main combustion chamber. This system was designed for about 25,000 psi and was hydrostatically tested at 9600 psi to insure safe operation up to 5000 psi.

Figure II-5 shows the end plate and the assembly attached to it. A Chromel electric wire was used to ignite the pellets. A photoresistor or photovoltaic cell was used to monitor the burning and to indicate when to turn the camera off. An Alumel-Chromel thermocouple was used to measure the inside temperature of the chamber.

b. Photographic System: A high-speed motion picture camera was used to photograph the burning of the pellets. As shown in Figs. II-3 and II-4, the camera was mounted on a rotary table allowing pictures to be taken of the pellet inside the chamber in one position and pictures of the title board in another position. Timing-light marks were recorded on the edge of the film every 1/120 second when the camera was operating.

c. Control Center: The control center mainly consisted of two variacs for changing the speed of the camera and the voltage across the hot wire, a pre-amplifier and a two-channel oscillograph for recording the outputs of the photocell and theremocouple. A potentiometer was also used to monitor the inside temperature of the chamber.

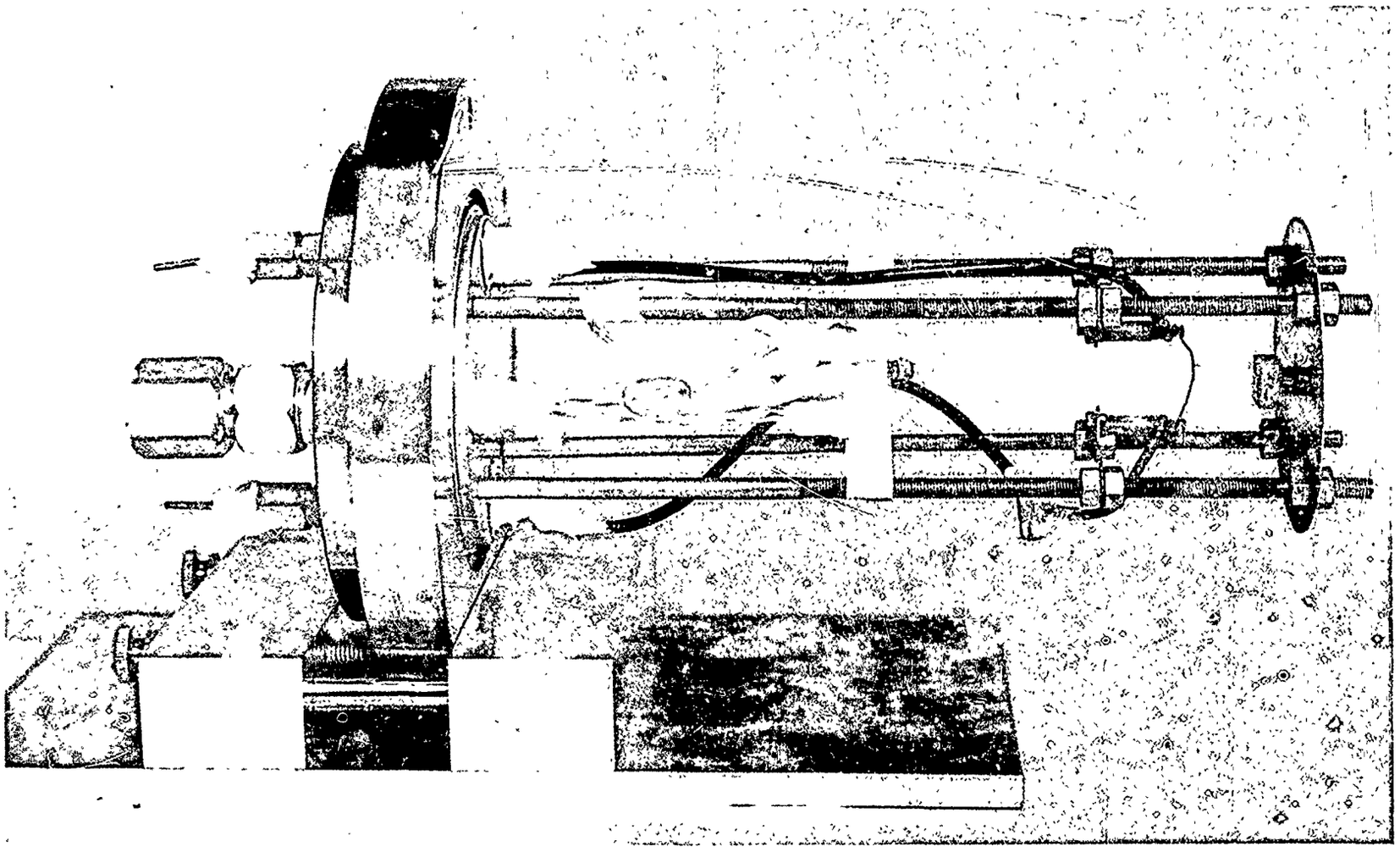


Figure II-5. "End plate" assembly with photocell, thermocouples, ignition wire, and a crystal mounted for ignition.

Experimental Procedure

There were four main steps in the experimental procedure: recrystallization, pelletizing, burning the pellets, and photographic analysis.

Recrystallization: To recrystallize ammonium perchlorate it was dissolved in distilled water to make a saturated solution at about 80°C (40 g AP in 100 g solution). Then the solution was heated to 90°C and filtered through a fine grade glass filter to remove the insoluble impurities. This filtration was done only in the first two recrystallizations of each "as received" sample. The clear solution was slowly cooled in a Dewar to room temperature (around 20°C) where the solubility is 18 g AP per 100 g of solution. These solubilities are reported by Ayerst and Phillips (2). Approximately 65% of the original ammonium perchlorate was recovered up to this stage. The recrystallized material was washed with the same volume of distilled water. The net recovery in each recrystallization was about 50%. Some of this material was used for further recrystallization and the rest was dried in an oven at 120°C. After drying the material carefully, it was ground and sieved through a series of stainless-steel Tyler standard sieves and the fraction having particle sizes between 88 and 175 microns (passing through 170 mesh and retained on 80 mesh) was separated for pelletizing. The sieved material was kept in a desiccator under vacuum until it was used to make the pellets.

Pelletizing: The die and the plungers were cleaned with acetone. The die was then filled with the dry ammonium perchlorate powder of particle size 80-175 microns to a level below the vacuum hole. Air inside the die was pumped out by connecting it to the vacuum line for about five minutes. Next, the die was placed in the press and the pressure was increased gradually to 100,000 psi. To avoid cracks in the pellet, the pressure was increased very slowly, especially at the end of the pressing. Finally the pressure was released and the pellet was pushed out by the upper plunger. One of the problems encountered was the binding of the pellets inside the die which made it difficult and sometimes impossible to remove the pellet from the die. Because of this difficulty, pellets longer than 2.5 cm were not made. At the pelletizing pressures above 100,000 psi some cracks appeared at both ends of the pellets. At these high pressures considerable friction developed between the pellets and the inside surface of the die which made it very difficult to push the pellet out.

Burning the Pellets: The length and weight of the pellets were measured. After cleaning the outside surface of the pellet, it was mounted on a steel block with a drop of Duco cement. This block was then mounted on the stand connected to the end plate of the combustion chamber, and the Chromel wire igniter was pressed against the top surface of the pellet. This assembly was then put in the combustion chamber, and the pellet location was adjusted in order to see the maximum length of the pellet through the camera. Next the electric wires and

the photocell and thermocouple terminals were connected and the chamber was pressurized with pure dry nitrogen. For runs at 1000 psig, a surge tank was also connected to the main chamber. About 15 minutes was allowed for the system to reach room temperature. During this period the camera was set to photograph the title board and then it was rotated and adjusted for photographing the burning. During burning the camera was operated at a speed of about 200 frames per second with the timing mark every 1/120 second. To start the test, the camera and the oscillograph were turned on and shortly after that the hot-wire igniter was also turned on. The beginning and the termination of deflagration could be seen on the output of the oscillograph in the form of two peaks. The first peak showed the ignition and the second showed the burning of the glue on the base of the pellet. After the burning was completed, the system was depressurized and the end plate assembly was taken out and cleaned.

Photographic Analysis: A moving picture projector was used to obtain data from the pictures. The "projected length" of the pellet versus the "frame number" and the "frame number" versus the "time" points were recorded for each run. Then the average linear burning rate was found from these data by a computer program which fitted the data to a straight line by the least-squares method. For most of the runs the burning rate was measured along two different lines and the average value found. Sometimes the burning surface was obscured by the shadow of the gaseous products. At 3500 psi this happened

more frequently and many runs were rejected because the burning surface could not be clearly seen.

Experimental Results

The deflagration rates of pressed pellets of ammonium perchlorate were measured at room temperature and under 1000 and 3500 psig ambient pressures. The ammonium perchlorate used for making pellets was 0 to 5 times recrystallized and was obtained from three manufacturers: Pennsalt Chemical Corporation, Matheson, Coleman and Bell and American Potash & Chemical Corporation. Hereinafter these three sources will be referred to respectively as "P", "M" and "A", and the degree of recrystallization will be shown by a number after each letter. The specifications available for the "as received" materials are shown in Appendix A.

The burning rates at room temperature were corrected to 21°C using the data reported by Watt (22). The extrapolation of Watt's data showed that the deflagration rate of ammonium perchlorate at temperatures around 20°C changed 1 percent per degree centigrade at 1000 psig and 2 percent per degree centigrate at 3500 psig.

The data obtained are plotted in Figs. II-6 to II-10. These plots show the change in deflagration rate versus degree of successive recrystallization. A summary of these data is also shown in Tables II-1 and II-2. The data in these tables represent an arithmetic average of all the corresponding experimental runs. A complete record of the data can be found in Appendix B.

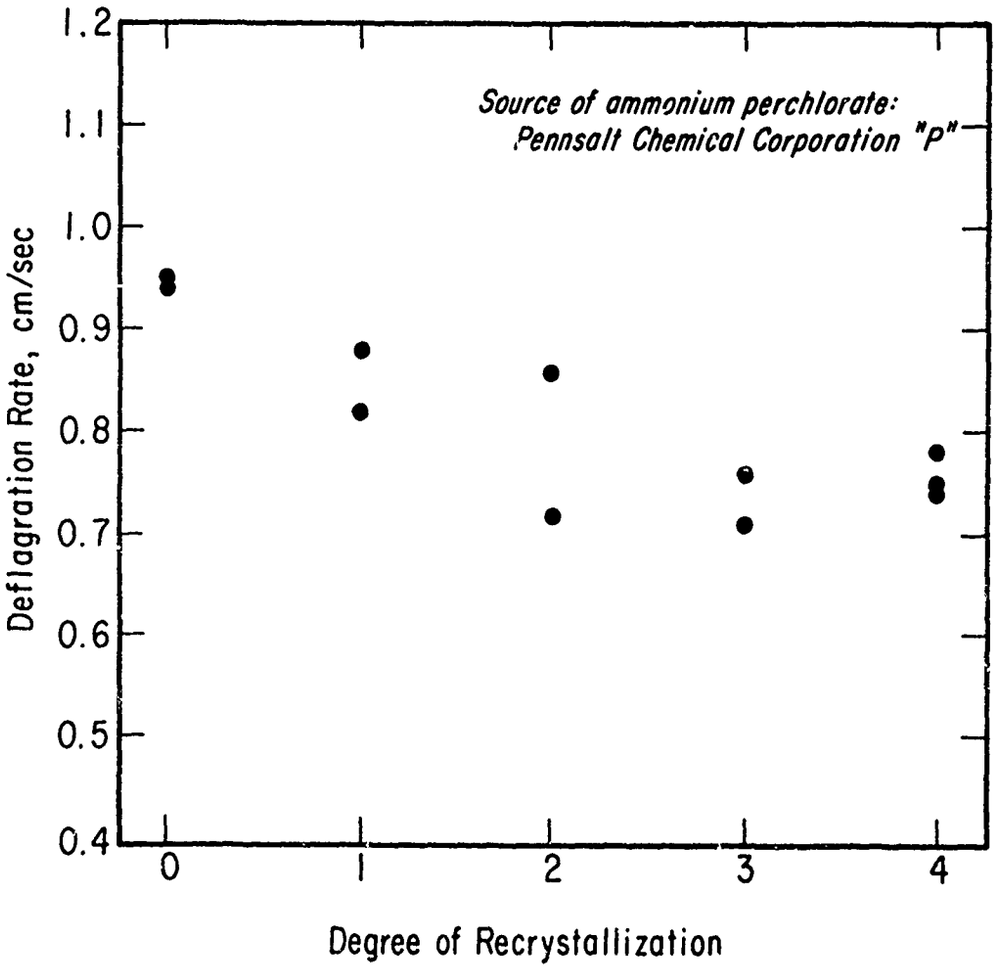


Fig. II-6. Deflagration rate of pellets of recrystallized ammonium perchlorate at 21°C and 1000 psig.

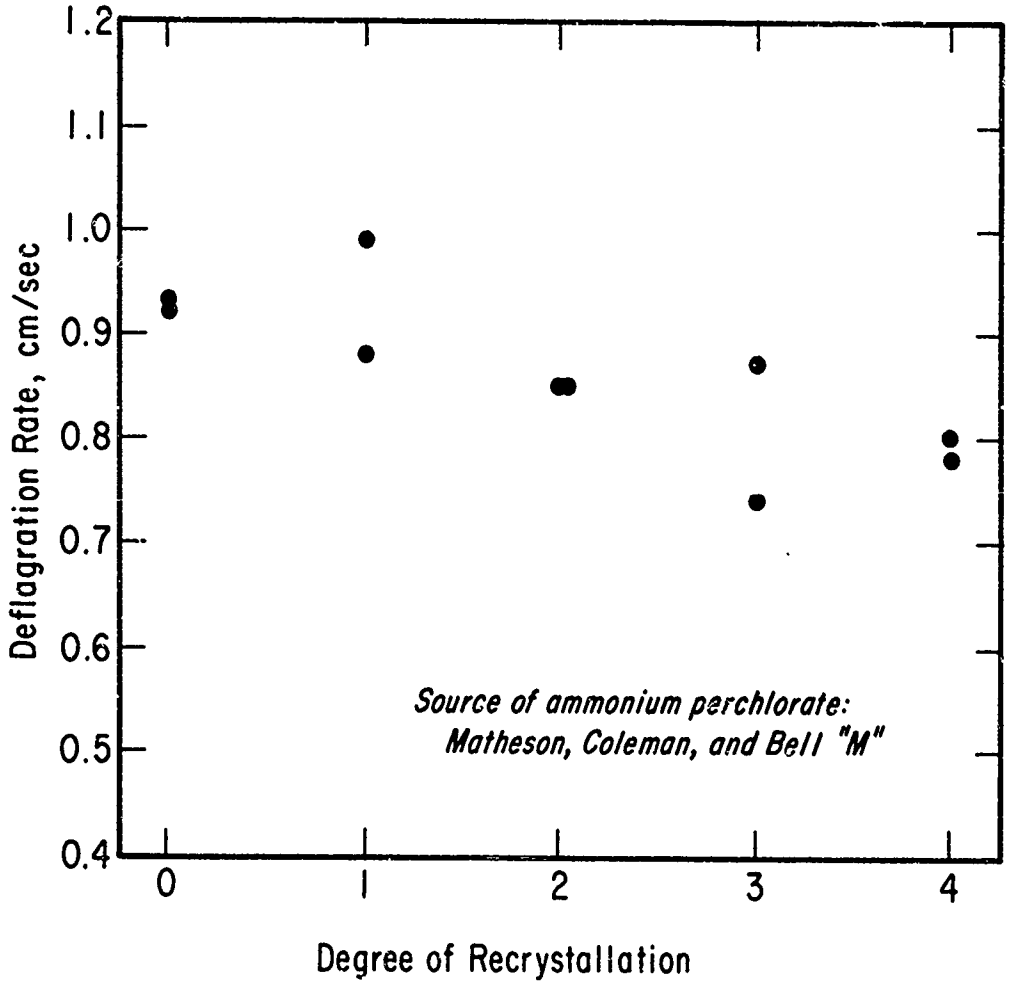


Fig. II-7. Deflagration rate of pellets of recrystallized ammonium perchlorate at 21°C and 1000 psig.

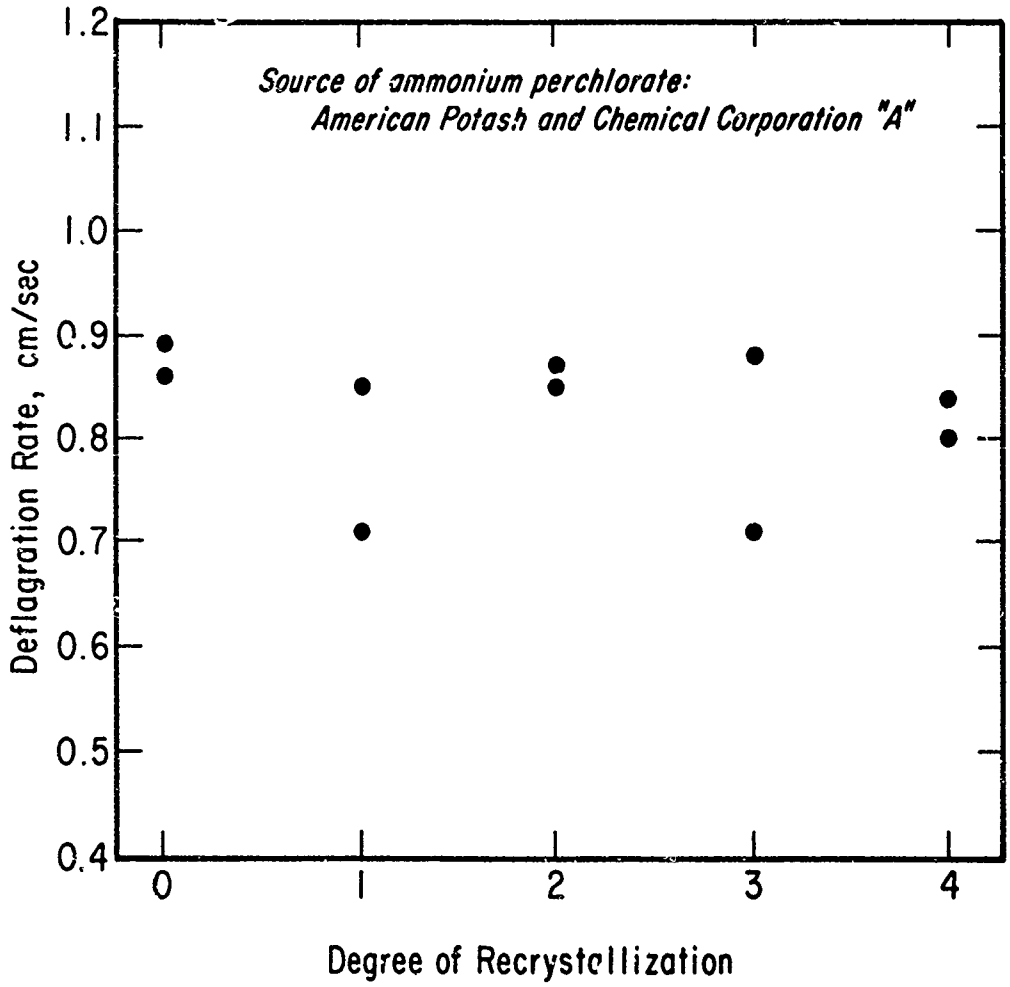


Fig. II-8. Deflagration rate of pellets of recrystallized ammonium perchlorate at 21°C and 1000 psig.

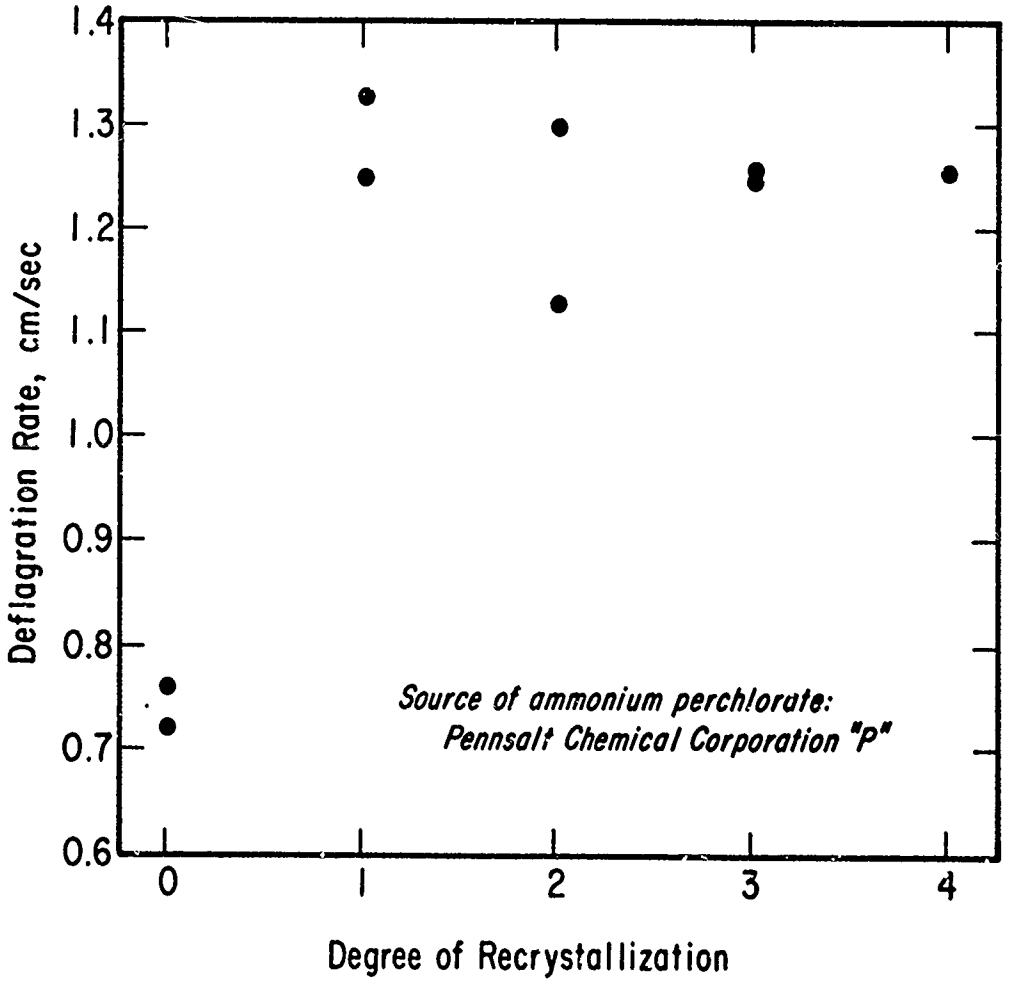


Fig. II-9. Deflagration rate of pellets of recrystallized ammonium perchlorate at 21°C and 3500 psig.

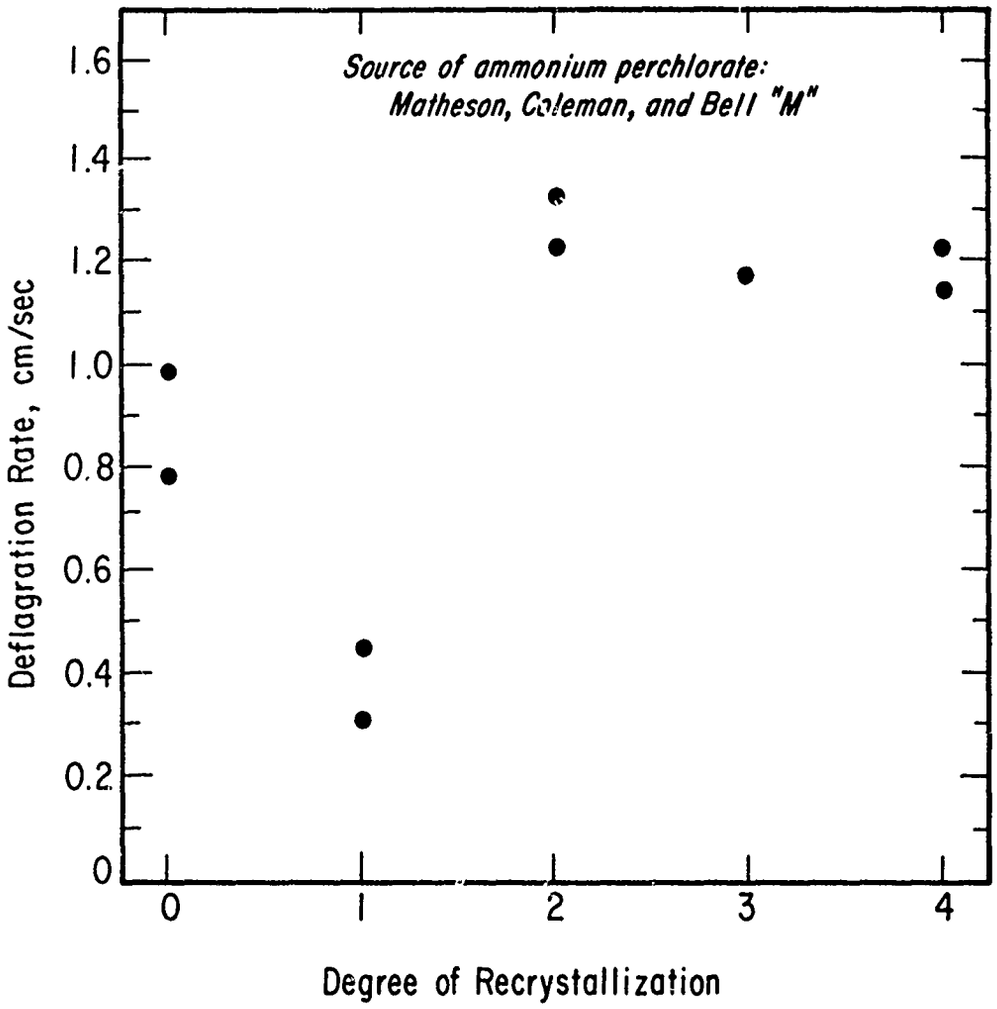


Fig. II-10. Deflagration rate of pellets of recrystallized ammonium perchlorate at 21°C and 3500 psig.

Table II-1

Average Deflagration Rate* of Polycrystalline Pellets of Ammonium Perchlorate at 1000 psig and 21°C

	Pennsalt (P) Deflagration rate cm/sec	Matheson (M) Deflagration rate cm/sec	American Potash (A) Deflagration rate cm/sec
As received	0.94	0.92	0.87
Once recrystallized	0.85	0.93	0.78
Twice recrystallized	0.79	0.85	0.86
Three times recrystallized	0.73	0.80	0.79
Four times recrystallized	0.76	0.79	0.82

*The data in this table represent an arithmetic average of all the corresponding experimental runs at 1000 psig.

Table II-2

Average Deflagration Rate* of Polycrystalline Pellets of Ammonium Perchlorate at 3500 psig and 21°C

	Pennsalt (P) Deflagration rate cm/sec	Matheson (M) Deflagration rate cm/sec
As received	0.74	0.88
Once recrystallized	1.29	0.38
Twice recrystallized	1.21	1.28
Three times recrystallized	1.25	1.18
Four times recrystallized	1.26	1.19

*The data in this table represent an arithmetic average of all the corresponding experimental runs at 3500 psig.

The effect of water inclusions on the deflagration rate of ammonium perchlorate was studied by burning a few pellets made from undried material. These pellets were glassy looking and almost transparent, while the pellets of dried material were white and opaque. The deflagration and propagation of burning surface in the moist pellets were more uniform and smoother than in dried pellets. It was found that the burning rate of dried "P1" was 0.85 cm/sec, while that of undried "P1" was 1.02 cm/sec, a difference of about 20%. However, no quantitative analysis of water content was made. A complete record of the experimental runs with undried ammonium perchlorate is given in Table B-3 of Appendix B.

Discussion of Results

The results of this study explain one of the factors which appears to be a major reason for the scatter of the existing data on the burning rate of ammonium perchlorate. As shown in Figs. II-6 to II-10, the burning rate changes when ammonium perchlorate is successively recrystallized. The change is considerable for the first two recrystallizations but becomes nearly negligible after the third. This indicates that impurities strongly affect the burning rate of ammonium perchlorate and this effect must be accounted for in order to obtain reliable data. As explained in Chapter I, most investigators have either used reagent grade ammonium perchlorate or have recrystallized it once or twice and have neglected the effect of the remaining impurities. Therefore it is

conceivable that an important reason for the scatter of the existing data is that the different investigators have used ammonium perchlorate containing traces of different impurities.

By successive recrystallizations many soluble impurities are removed easily. Compounds which are isomorphic to ammonium perchlorate cannot be readily removed by successive recrystallization, and in general the concentration of these compounds approaches a limit. This limit is zero only if the concentration of isomorphic impurities in the crystallized phase is less than that in the saturated solution during each recrystallization. Therefore the burning rate of a special type of ammonium perchlorate may change by successive recrystallizations but should finally approach a limit. It follows, also, that this limit may not be the same for ammonium perchlorate from different sources which contain different types of impurities.

The final burning rate (approaching limit) for the three sources of ammonium perchlorate used in this study are almost the same. This means either the limiting concentrations of the effective impurities were the same for the recrystallized ammonium perchlorate from these three sources, or the successive recrystallizations decreased the concentration of the effective impurities to a negligible amount. If the second case is true, the final burning rate is the intrinsic burning rate of pure ammonium perchlorate. This case is more probable than the first, although its validity can only be examined

by accurate analytical tests for detecting impurities.

It is important to note that in Figs. II-6 to II-10 the "degree of recrystallization" is not really a suitable variable, because the effectiveness of impurity removal by one recrystallization is largely dependent on the method used. However, this was chosen as the abscissa in these plots because no better quantitative measure of the impurities was available.

Another interesting result is the change in the effect of impurities with change in pressure. Comparison of the data at 1000 psig and 3500 psig shows that the impurities have a much stronger effect at 3500 psig. It is worthy of note that the scatter of data in the literature at pressures around 3500 psig is also much greater than that at 1000 psig. The results obtained also show that the effect of the type of impurity may also change with pressure. For example, the impurities in the "as received" ammonium perchlorate used in this study have a net positive catalytic effect at 1000 psig but a net inhibitor effect at 3500 psig. At 3500 psig there is no distinguishable maximum or minimum in the plots and the fluctuations are almost within the accuracy of the results; but at 3500 psig the burning rate of "P" increases to a maximum and that of "M" passes through a maximum and a minimum before leveling off.

A maximum and minimum in the burning rate indicates a catalyst-inhibitor interaction. At a certain pressure some impurities are positive catalyst and others are inhibitors.

When ammonium perchlorate is recrystallized the relative concentration of these species changes. Therefore the net effect can change from positive to negative values in the course of recrystallization. This results in the maximum and minimum in the burning rate.

The mechanism by which the catalysts change the burning rate and the reason for the strong influence of the pressure are not definitely known, and various theories are proposed. Some investigators believe that catalysts mainly affect the kinetics of the reactions occurring in combustion. Others have reported that catalysts change the burning rate mostly by changing the rate of radiative heat transfer because of their effect on the optical properties of the gas phase and the burning surface. However, both factors may interact and their relative importance may change with pressure.

It was found that water inclusion in ammonium perchlorate increases the burning rate considerably. It is notable that Bircumshaw (3,4) and Svetlou and Koroban (20) have reported that water also increases the decomposition rate of ammonium perchlorate. Most investigators who have studied the burning of pellets have not reported drying the ammonium perchlorate before pelletizing. This may also be a reason for the difference in published results.

Another possible source of scatter of the data is the difficulty in making pellets of identical physical structure. Sometimes a difference of 25% is observed between the burning rates of two pellets from the same material (19). This can

only be accounted for by difference in physical structure of the pellets. The effect of particle size on the burning rate has been studied by Shannon (16,17,18) but there are many other factors related to the structure of the pellets which have not been studied. For example, the pelletizing pressure may influence the burning rate. The density distribution may also change when the dimensions of the die or the pelletizing pressure is changed; completely uniform distribution of pressure in the pellets cannot be obtained during pelletizing. Shannon (16) and Smith (19) reported that under 100,000 psi pelletizing pressure the maximum average density, 1.9 g/cm^3, is obtained. It was found that the density can be increased to 1.94 g/cm^3 by pressing the powder in a floating-type vacuum die. Sometimes minute cracks were observed in some pellets, especially at both ends. These pellets were rejected for this study because the cracks could change the burning rate and probably were the reason for the sudden extinction observed by Smith (19).

Another possible reason for the disagreement among investigators is some inconsistency in measuring the average burning rate of pellets from photographic analysis. Although this is not as important as the factors already discussed, it nevertheless should be considered when the results of different investigations are compared. The burning rate, or in other words the propagation velocity of the flame, should be measured along a line perpendicular to the burning surface. This measurement is difficult because the burning surface is

projected as a curve in the movies and usually changes its shape and curvature during the deflagration of the sample. This problem mostly exists in the burning of polycrystalline pellets, which do not burn as uniformly and smoothly as do single crystals. Different methods can be used to measure the propagation rate of deflagration flame along a pellet. Length measurements can be made by considering an "average modified burning surface". This means replacing the projected burning surface, which is a curve, by the best straight line perpendicular to the axis of the pellet. Another method is to measure the length along a fixed line parallel to the axis of the pellet. It was found that the second method is more reproducible; therefore it was used throughout this study. To minimize the error, the rate was measured along two or three different lines separately and then the average was found for each run. After measuring the length and time points, one can use different methods for finding a linear average rate. Three possible methods are:

(a) Taking one point at each end of the pellet and dividing the distance between these two points by the corresponding burning time.

(b) Plotting "length points" versus "time points" and measuring the slope of the linear portion of the curve. Using this method one can eliminate the nonlinearity due to the transient effects.

(c) Fitting all the length and time points to a straight line using the least-squares method.

A typical comparison of the results obtained by these three methods in two experimental runs is shown in Figs. II-11 and II-12. In most cases the rate obtained by method (c) was found to lie between that found by (a) and (b). In this study method (c) was used to find the average linear deflagration rate.

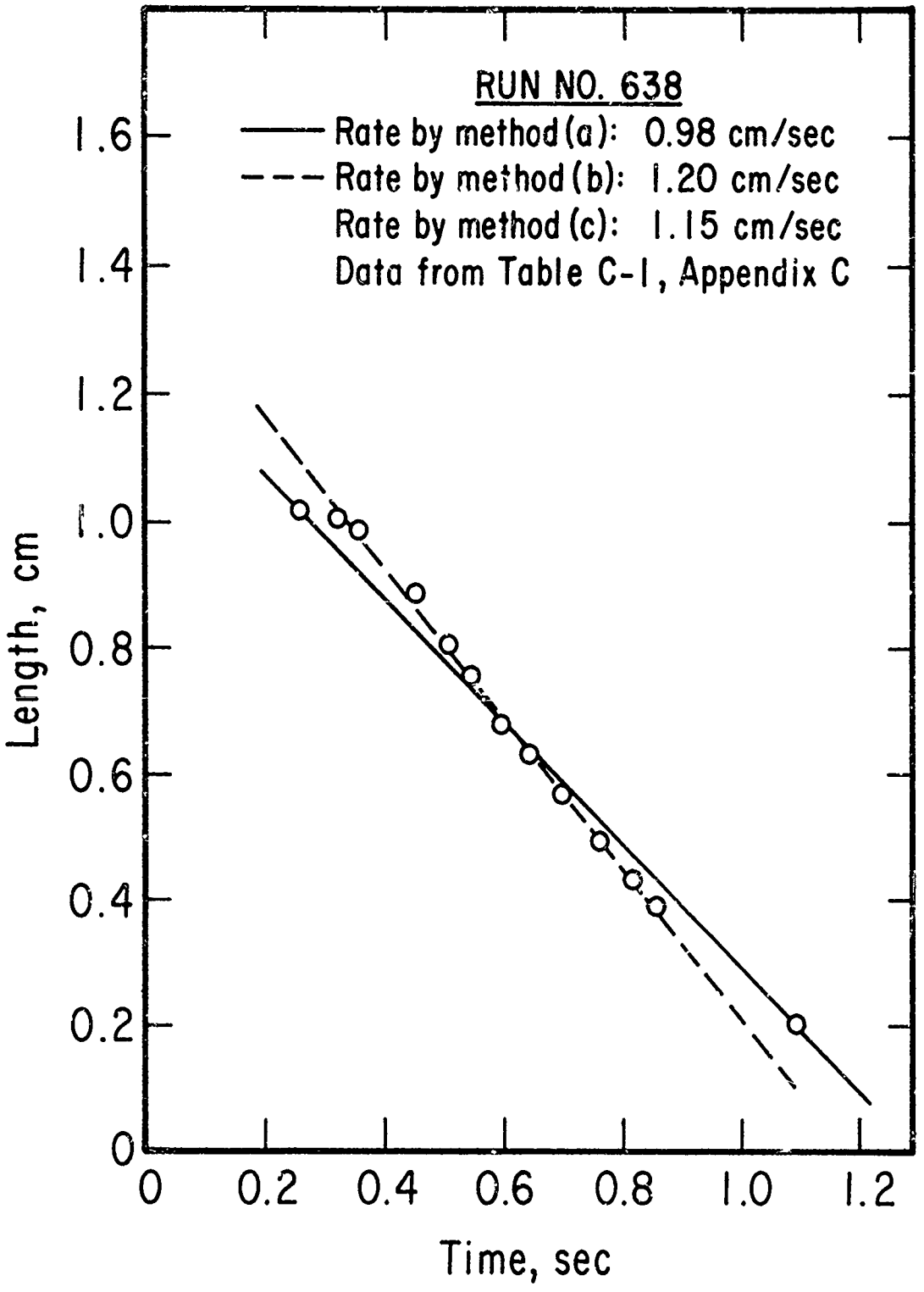


Figure II-11. Measurement of the average deflagration rate from the results of photographic analysis.

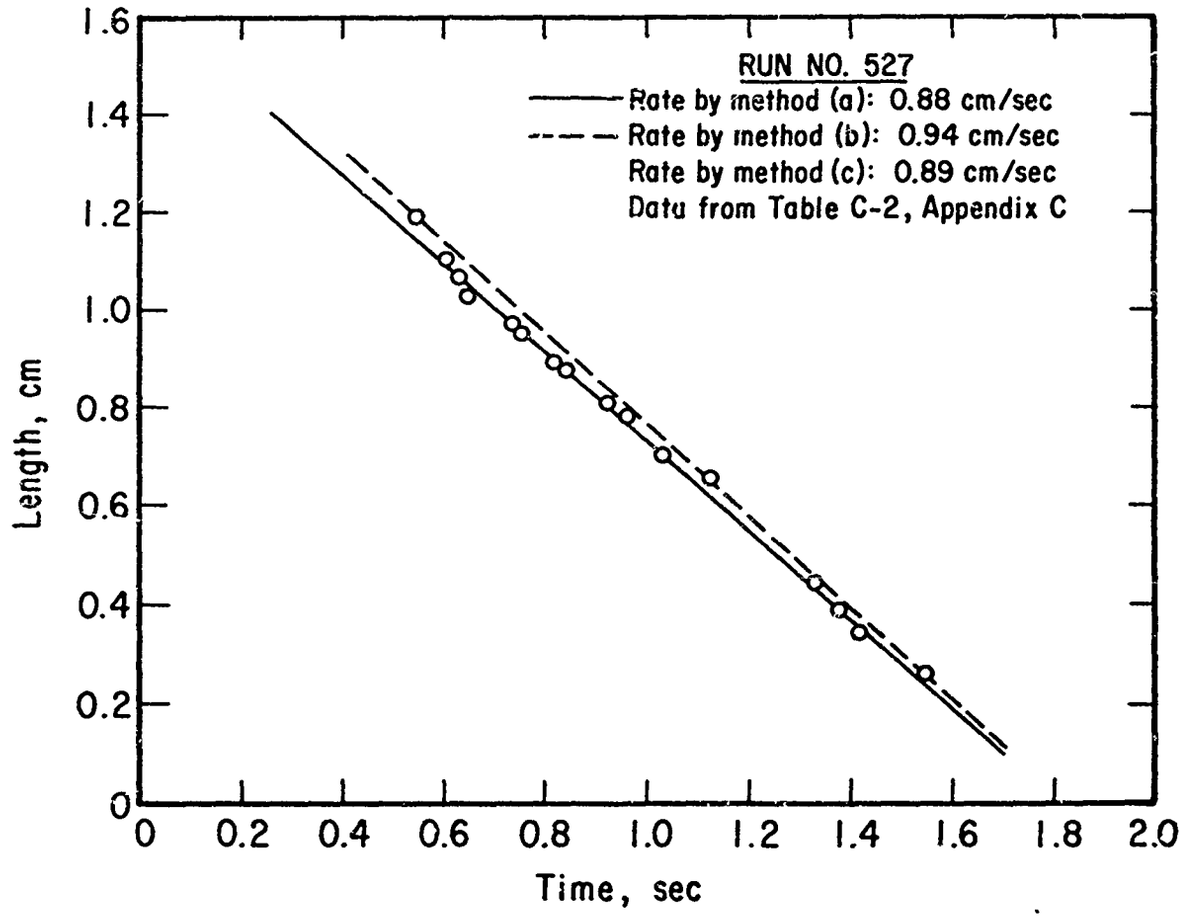


Fig. II-12. Measurement of the average deflagration rate from the results of photographic analysis.

Conclusions and Recommendations

The results of this study show that impurities influence the burning rate of ammonium perchlorate and no reliable data can be obtained without careful consideration of this effect. Successive recrystallization removes most of the imputities but it is not known whether all impurities can be removed in this way. Some of the impurities may be isomorphic to ammonium perchlorate and their concentration may approach a constant limit instead of going to zero. In this study the burning rates of ammonium perchlorate from three different sources approached the same limit with successive recrystallization. This indicates a strong probability that the limit is the intrinsic burning rate of pure ammonium perchlorate.

Although the nature of the impurities and their concentrations were not determined, the results suport the interpretation that both catalysts and inhibitors were present in the "as received" ammonium perchlorate. Since in successive recrystallizations the positive and negative catalytic impurities were not necessarily removed at the same rate, in some cases the burning rate versus the degree of recrystallization was not monotonic but passed through a maximum or minimum before approaching an asymptote. Moreover, the effect of impurities changed with the changes in the total deflagration pressure and was greater at high pressure.

These results suggest that one of the important reasons for the scatter of the existing data on the burning

rate, especially at high pressures, is that different investigators have not purified ammonium perchlorate to the same degree and some of them have presumed that the remaining traces of impurities have not affected their results.

In addition to the effect of impurities, the burning rate of polycrystalline pellets is possibly influenced by some other factors which are related to the physical structure of the pellets such as particle size, pelletizing pressure, density distribution in the pellets, and air in the void volume between the particles. The quantitative effects of many of these factors are not yet known. The difficulty in controlling all of these factors is another possible source of scatter of the existing data in the literature. In this study a floating type vacuum die was designed and used to improve this uniformity of the pellet structure.

A preliminary study on the effect of water inclusions in pellets showed that the deflagration rate of moist ammonium perchlorate was higher than that of dried powder. It was also found that water content changes the physical structure of the pellets and clear pellets can be made from moist powder in a vacuum die. The effect of water, which has been neglected by most of the investigators, may be another source of disagreement in the burning-rate data.

On the basis of the present study, the following areas are suggested for future research on this subject.

a. A quantitative and qualitative analysis of the impurities existing in ammonium perchlorate seems to be the

next step in the study of impurities. This analysis should be mainly done on the "as received", once and twice recrystallized ammonium perchlorate because the effect of impurities is considerable in this range. Such a study would be helpful in further interpretation of the results obtained in the present study.

b. Up to this time, deflagration rate data from single crystals have been more reproducible than similar data obtained by burning pressed pellets. Moreover, single crystals offer advantages in the study of catalysts which are isomorphic to ammonium perchlorate because of the very uniform distribution of the catalyst in a doped crystal. It is therefore suggested that single crystals be used for the following two types of investigations which are closely related to each other.

The first investigation should be a more accurate analysis of the effect of natural impurities by burning single crystals which are grown from solutions of ammonium perchlorate having different degrees of recrystallization. In general these crystals will contain different amounts of isomorphic impurities. This would be similar to the present study on pressed pellets but would hopefully give more accurate and less scattered data. Such a study is especially suggested for the first two recrystallizations.

The second investigation should be on the deflagration of crystals doped with known added catalysts. Of course the only catalysts which can be used in such a study are those

compounds which are isomorphic with ammonium perchlorate. The results of such a study should be compared with the deflagration rate of pressed pellets made from ammonium perchlorate mechanically mixed with the catalysts or made from the powder obtained by co-crystallization of ammonium perchlorate and the catalysts.

c. More detailed study of the factors related to the physical structure of the pellets (such as density, particle size, pelletizing pressure, etc.) and their effects on the deflagration rate, although not easy, would be helpful in making uniform pellets of more reproducible quality and would also help in comparing the deflagration of single crystals with that of pressed pellets.

d. Clear pellets which were made in this study have some desirable qualities of single crystals such as burning with a uniform and smooth propagation of flame zone. They are also much easier to make than single crystals. Thus, by controlling the water content of these pellets it might be possible to use them in many deflagration studies on ammonium perchlorate, especially where single crystals cannot be used such as for the studies with catalysts which are not isomorphic to ammonium perchlorate. Therefore a study on the structure of these pellets would also be valuable.

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CHAPTER III

EFFECTIVENESS FACTOR FOR SURFACE DIFFUSION AND REACTION ON CATALYST SURFACE*

Introduction

Considerable experimental evidence exists which indicates that the distribution of catalyst has relatively little effect on its performance. That is, mechanical mixtures of catalyst and propellant pressed into pellets appear to give about the same effect as catalysts isomorphically substituted into the propellant crystal lattice. Obviously, the performance cannot be entirely independent of the distribution and accordingly theoretical study of the effects of distribution and the important parameters needed to describe the behavior of catalyst-propellant mixtures was carried out. The system is similar mathematically to a well-known problem of simultaneous diffusion and chemical reaction in porous catalysts -- the Thiele-Zeldovich problem [15,20].

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* To appear as a paper by H. Y. Sohn, R. P. Merrill and E. E. Petersen in Chem. Eng. Sci., 1970.

Since the concept of the "effectiveness factor" of a porous catalyst was introduced by Thiele [15], its calculation has been modified, generalized, and extended for different reaction mechanisms, for different pellet geometries [10,12,18, 19] and for nonisothermal catalyst particles [1,10,17]. This work is for the case of a porous catalyst-pellet, where reactant molecules diffuse through the void pore spaces of the pellet and undergo catalytic reaction.

The same concept can be applied to surface reaction which is coupled with surface diffusion. Surface diffusion refers to the migration of atoms or molecules adsorbed on a solid surface under a concentration gradient in the surface plane. Detailed reviews of surface diffusion are available elsewhere [2,4].

There is evidence that migration of species adsorbed on solid surfaces plays an important role in catalysis, especially in the case of some reactions involving dual-function catalysts [3,13]. Sinfelt and Lucchesi [13] have shown the cooperative action of Pt and Al_2O_3 centers of Pt–Al_2O_3 catalyst in the hydrogenation of ethylene, and concluded that this cooperative effect is due to the migration of reactive intermediates between the two centers. Since Pt or Al_2O_3 alone has a low catalytic activity compared with Pt-Al_2O_3 catalyst, and Pt and Al_2O_3 are good adsorbents of H_2 and ethylene, respectively, the possibility that Pt centers produce hydrogen atoms which migrate to the

Al_2O_3 surface to react with chemisorbed ethylene has been suggested.

A mathematical model to describe the combined effect of surface diffusion and intrinsic reaction rate on a solid surface is proposed, and an analytic solution to the first-order reaction case and an exact numerical solution and approximate solution to the second-order reaction case are presented.

MODEL AND MATHEMATICAL FORMULATION

The model assumes the catalyst surface to be made up of uniformly distributed adsorption centers, or islands of one metal on a homogeneous surface of a second metal or other support. The adsorption centers, or islands, are assumed to be circles with a radius R_i and are located at a distance $2R_o$ from each other. In the case of discrete atomic adsorption sites R_i is the order of the crystal radius of the catalytic solid. Fig.III-1 shows such a surface.

Suppose a reactant A is adsorbed on the adsorption centers and diffuses away along the surface where it reacts either with another reactant B in gas phase or by itself. If the system is isothermal and the rate obeys simple power-law kinetics, the mass balance equation is:

$$\frac{d^2C}{dr^2} + \frac{1}{r}\frac{dC}{dr} - \frac{k_n}{D_s} C^n = 0 \qquad (1)$$

where C = surface concentration of diffusing reactant,

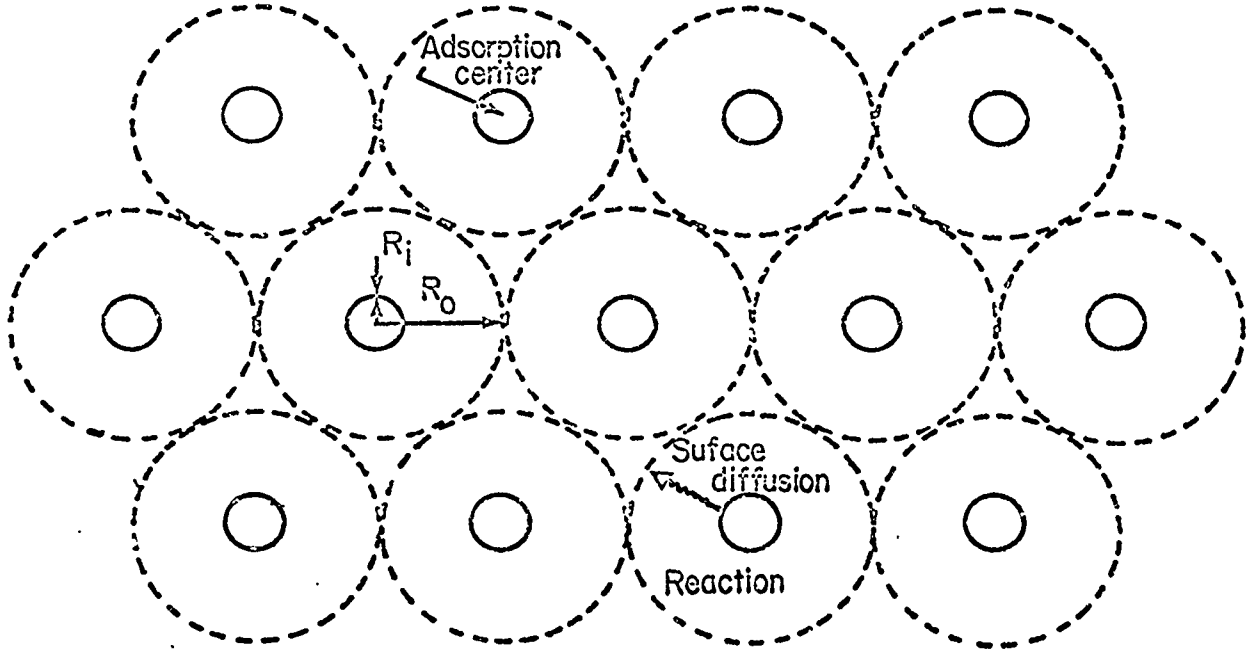

Fig. III-1. Surface with uniformly distributed adsorption centers.

r = distance from the center of an adsorption center,

n = intrinsic reaction order,

k_n = nth-order intrinsic surface reaction rate constant,

D_s = surface diffusivity.

Equation (1) is subject to the boundary conditions:

$$\left.\begin{aligned} C &= C_o && \text{at } r = R_i \\ \frac{dC}{dr} &= 0 && \text{at } r = R_o \end{aligned}\right\} \quad (2)$$

The adsorption is assumed fast on the centers but very slow on the active support so that the concentration on the support-surface along the edge of the adsorption center is in equilibrium with the gas phase and maintained constant at C_o for constant gas-phase pressure and temperature. The reactant A can reach the active area of the catalyst only by diffusion from the adsorption centers. The possibility of such diffusion from an adsorption center to the surface of a support has been shown by Robell et al. [11] for a system consisting of platinum centers on a carbon surface.

For a constant D_s Eq. (1) may be rewritten in dimensionless form:

$$\frac{d^2\psi}{d\eta^2} + \frac{1}{\eta}\frac{d\psi}{d\eta} - \sigma_n^2 \psi^n = 0 \quad (3)$$

where

$$\left.\begin{aligned} \psi &= C/C_o \\ \eta &= r/R_i \\ \sigma_n &= R_i \sqrt{\frac{k_n C_o^{n-1}}{D_s}} \end{aligned}\right\} \quad (4)$$

and the boundary conditions become

$$\left.\begin{aligned} \psi &= 1 && \text{at} \quad \eta = 1 \\ \frac{d\psi}{d\eta} &= 0 && \text{at} \quad \eta = \eta_o = R_o/R_i \end{aligned}\right\} \tag{5}$$

The dimensionless parameter σ_n (which henceforth will be called the "surface-diffusion modulus") is the two-dimensional equivalent for the proposed system of the Thiele parameter [10,15].

As usual, it is expected that the solution may be presented as the effectiveness factor versus the surface-diffusion modulus. The effectiveness factor $\mathcal{E}_n$ for the proposed model is defined as

$$\mathcal{E}_n \equiv \frac{\text{actual rate of reaction}}{\text{rate in the absence of a concentration gradient}} = \frac{-2 \left.\frac{d\psi}{d\eta}\right|_{\eta=1}}{(\eta_o^2 - 1)\,\sigma_n^2} \tag{6}$$

SOLUTION FOR A FIRST-ORDER SURFACE REACTION

When the surface reaction is of first order ($n = 1$), the analytic solution to Eq. (3) is possible and the dimensionless gradient at the interface is found to be

$$\left.\frac{d\psi}{d\eta}\right|_{\eta=1} = \sigma_1 \, X \, \frac{I_1(\sigma_1) K_1(\sigma_1\eta_o) - I_1(\sigma_1\eta_o) K_1(\sigma_1)}{I_o(\sigma_1) K_1(\sigma_1\eta_o) + I_1(\sigma_1\eta_o) K_o(\sigma_1)} \tag{7}$$

where σ_1 = surface-diffusion modulus for first-order surface reaction, and

I_j, K_j = modified Bessel functions of the first and second

kinds, respectively, with the subscripts designating the order.

The effectiveness factor, in this case ε_1, is obtained by substituting Eq. (7) intc Eq. (6). A plot of ε_1 is shown in Fig. 2. A generalized surface-diffusion modulus, $\hat{\sigma}_n$, is used as the abscissa in Fig. 2, for reasons given in the following section. Note, however, that $\hat{\sigma}_1$ is equal to σ_1. The dashed line in Fig III-2 is the asymptotic solution of the effectiveness factor as σ_1 approaches infinity. For a first-order reaction the asymptotic solution from Eqs. (6) and (7) is

$$(\varepsilon_1)_{\sigma_1 \to \infty} = \frac{2}{(\eta_o^2 - 1)\,\sigma_1} \qquad (8)$$

It will be shown in the following section that this is a special case of the general form of asymptotic solutions for nth-order reactions.

EXACT NUMERICAL SOLUTION AND APPROXIMATE SOLUTION FOR A SECOND-ORDER SURFACE REACTION

For a second-order reaction the exact analytic solution of Eq. (3) could not be obtained and other means of computation were employed. An analog computer with a careful programming, such as that used by Tinkler and Metzner [16] in solving the problem of nonisothermal porous catalysts, would probably yield solutions. In the present work, however, the problem was solved numerically using a digital computer.

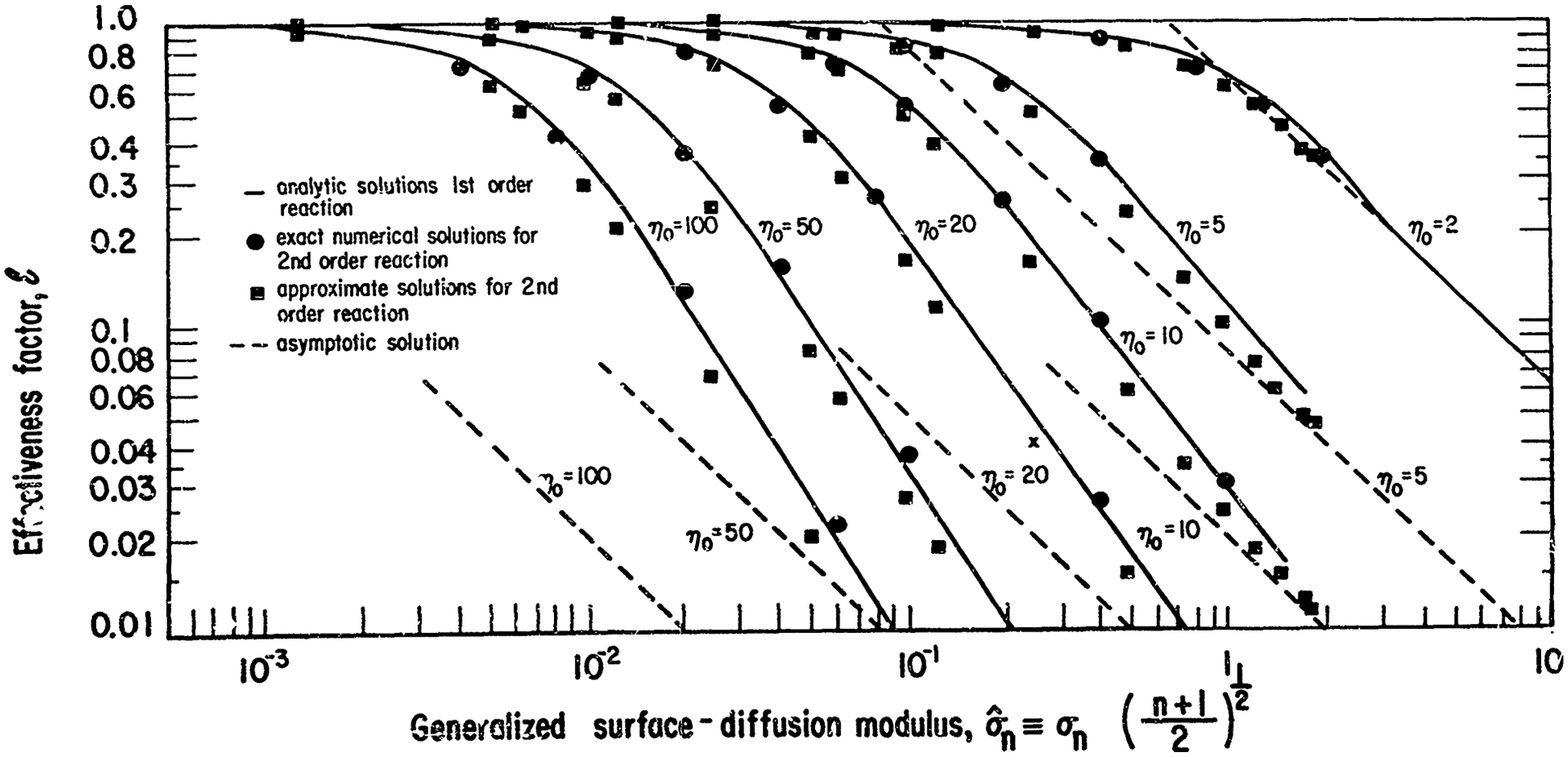

Fig. III-2. Effectiveness factor for integral-order reactions on a catalyst surface as a function of the generalized surface-diffusion modulus.

The two-point boundary value problem of Eq. (3) was converted to an initial value problem, i.e. a gradient at $\eta = 0$ is assumed and integration performed to find the value of $d\psi/d\eta$ at $\eta = \eta_c$. The solution can be bracketed within any desired accuracy after a few trials. The Adams method was used for the integration [5]. The results are shown in Fig. III-2. The effectiveness factor $\mathcal{E}$ is plotted against the generalized surface-diffusion modulus $\hat{\sigma}_n$, which is defined as

$$\hat{\sigma}_n \equiv \left[\frac{n+1}{2}\right]^{1/2} \sigma_n$$

The reason for using $\hat{\sigma}_n$ will become apparent when the asymptotic solution as $\hat{\sigma}_n \longrightarrow \infty$ for the nth-order reaction is examined.

In a system with a large value of σ_n the reaction mostly occurs near the edge of an adsorption center and Eq. (3) becomes approximately [9,10]

$$\frac{d^2\psi}{d\eta^2} - \sigma_n^2 \psi^2 = 0 \tag{9}$$

with new boundary conditions

$$\left.\begin{aligned} \psi &= 1 && \text{at } \eta = 1 \\ \frac{d\psi}{d\eta} &= 0,\ \psi = 0 && \text{as } \eta \longrightarrow \infty \end{aligned}\right\} \tag{10}$$

The solution is possible for any value of $n \geq 0$, and the effectiveness factor is given by

$$(\mathcal{E}_n)_{\sigma_n \to \infty} = \frac{2}{(\eta_o^2 - 1)\sigma_n}\left(\frac{2}{n+1}\right)^{1/2}$$

or

$$(\varepsilon_n)_{\hat{\sigma}_n \to \infty} = \frac{2}{(\eta_o^2 - 1)\,\hat{\sigma}_n} \qquad (11)$$

This asymptotic form suggests the use of $\hat{\sigma}_n$ in plotting the effectiveness factor in order to bring the asymptotes for different reaction orders on one line for each value of η_o. It is also known for slab geometry that the exact values of ε_n for first- and second-order reactions lie in approximately the same position when such a generalized form of the Thiele parameter is used [10].

As can be seen in Fig. III-2, the solutions for the second-order reaction lie very close to those for the corresponding first-order reaction, thus confirming the usefulness of the generalized parameter in the present case also. It should be noted that for small values of η_o, i.e. < 20, the solutions rapidly approach the corresponding asymptotes. For large values of η_o, i.e. > 50, however, the asymptotic solutions yield good approximations to the real solution only at very low values of the effectiveness factor.

It can also be seen that the ratio of the radii, η_o, plays an important role in the kinetics of reactions on such surfaces. Although the effectiveness factor itself (based on the surface area of the support) decreases as η_o increases, the actual rate of reaction per unit surface area of the adsorption center, as given below, generally increases with η_o.

$$\left.\begin{array}{l}\text{Rate of reaction per unit} \\ \text{area of adsorption center}\end{array}\right\} = v = \varepsilon_n(\eta_o^2 - 1)\, k_n\, c_o^n \tag{12}$$

The limiting forms of this rate are

$$v = (\eta_o^2 - 1)\, k_n\, C_o^n \qquad \text{for small } \hat{\sigma}_n \tag{13a}$$

$$v = \frac{2}{\hat{\sigma}_n}\, k_n\, C_o^n = \frac{2}{R_i}\left(\frac{2}{n+1}\right)^{1/2}\left(k_n D_s\right)^{1/2} C_o^{\frac{n+1}{2}} \qquad \text{for large } \hat{\sigma}_n \tag{13b}$$

Therefore, using small islands (small R_i) gives better utilization of the adsorption material and is recommended when this material is valuable, as in the case of Pt–alumina reforming catalysts. Of course, large islands would be used when the opposite is true.

Note from Eq. (13b) that, as $\hat{\sigma}_n$ approaches infinity,

$$\text{Reaction rate} \propto (k_n D_s)^{1/2} \tag{14}$$

Since surface diffusion is considered to be an activated process [e.g. 4,6,11] and its temperature dependence is given by the expression

$$D_s = D_o e^{-E_d/RT},$$

where D_o is a constant independent of temperature and E_d is the activation energy for surface diffusion, Eq. (14) implies that the apparent activation energy will become the arithmetic average of the activation energies of intrinsic reaction and of diffusion:

$$E_{app} = \frac{E_r + E_d}{2} \tag{15}$$

where E_r = activation energy of intrinsic surface reaction. Since E_r and E_d usually differ, the temperature dependence of a diffusion-controlled surface reaction for a large $\hat{\sigma}_n$ can be quite different from that of the intrinsic surface reaction and could conceivably be greater than E_r in special cases. The change in the apparent activation energy in this case can be compared with that for a porous catalyst where for a large

Thiele parameter the apparent activation energy is equal to one-half the true activation energy [10]. Equation (15) gives just this result if E_d is very small, as is the case for the gas phase region where $D \propto T^{1/2}$ (Knudsen diffusion) or $D \propto T^{3/2}$ (bulk diffusion).

Equation (13b) also shows that the apparent reaction order is changed:

$$\text{Apparent reaction order} = \frac{n+1}{2} \qquad (16)$$

This change is the same as in the case of porous catalyst in the diffusion-influenced region [10],

The combined effect of reaction and surface diffusion with the concomitant changes in the apparent activation energy and the reaction order can have an important influence on selectivity of a catalyst analogous to the case of a porous catalyst [10,19].

The effectiveness factor, as a function of the surface-diffusion modulus, σ_n, approaches the asymptote from above, whereas the approach is from below for the porous catalyst with a geometry of slab, cylinder or sphere [10]. Apparently this occurs for the following reason: When σ_n approaches infinity, the reaction rate is much faster than the diffusion rate; hence the reaction occurs within a narrow region along the edge of the adsorption center, where there is no effect of curvature on the concentration gradient. If diffusion occurs away from the center of a cylinder or sphere in a system with a σ_n smaller than infinity, the expanding coordinate will cause the gradient

at the interface to become larger than for a slab. This, in turn, gives a larger effectiveness factor. When diffusion occurs toward the center, the contraction of the coordinate gives the opposite effect.

An approximate solution has also been obtained by linearizing the differential equation and is shown in Fig. 2 for purposes of comparison. When σ_n approaches zero the solution of Eq. (3) with boundary conditions given by Eqs. (5) is obviously $\psi = 1$.

Assume the following expression for ψ for a small value of σ_n:

$$\psi = 1 + \Delta\psi \tag{17}$$

where $\Delta\psi$ is a small perturbation term which vanishes as σ_n approaches zero. Substituting Eq. (17) into Eq. (3) and neglecting higher order terms than $\Delta\psi$, one obtains

$$\frac{d^2\,\Delta\psi}{d\eta^2} + \frac{1}{\eta}\,\frac{d\,\Delta\psi}{d\eta} - \sigma_n^2\,(1 + n\Delta\psi) = 0 \tag{18}$$

with boundary conditions

$$\begin{aligned} \Delta\psi &= 0 && \text{at } \eta = 1 \\ \frac{d\Delta\psi}{d\eta} &= 0 && \text{at } \eta = \eta_o \end{aligned} \tag{19}$$

The gradient at the interface for a second-order reaction ($n = 2$) is now given as

$$\left.\frac{d\psi}{d\eta}\right|_{\eta=1} = \left.\frac{d\Delta\psi}{d\eta}\right|_{\eta=1} = \frac{\sigma_2}{\sqrt{2}} \times \frac{I_1(\sqrt{2}\,\sigma_2)\,K_1(\sqrt{2}\,\sigma_2\eta_o) - I_1(\sqrt{2}\,\sigma_2\,\eta_o)\,K_1(\sqrt{2}\,c_2)}{I_o(\sqrt{2}\,\sigma_2)\,K_1(\sqrt{2}\,\sigma_2\eta_o) + I_1(\sqrt{2}\,\sigma_2\,\eta_o)\,K_o(\sqrt{2}\,\sigma_2)} \tag{20}$$

where σ_2 is the surface-diffusion modulus for second-order surface reaction. The effectiveness factor obtained using this approximate solution is plotted in Fig. ———————————

The approximate solution for the present model agrees fairly well with the exact solution over a wide range of effectiveness factor, although a calculation [14] shows that the classical perturbation solution, with σ_n^2 as the perturbation parameter, of the form

$$\psi = \psi_o + \sigma_n^2 \psi_1 + \sigma_n^4 \psi_2 + \cdots\cdots \qquad (21)$$

rapidly deviates from the exact solution as soon as the effectiveness factor departs from unity.

Also, when the effectiveness factor is not very small, between 1 and 0.6, the approximate solution gives a better closed-approximation to the exact solution than the solution for first-order gives, although at lower values of the effectiveness factor the first-order solution does better. In fact the approximate solution does not give the correct asymptotic form as σ_2 approaches infinity. From Eq. (20) one can see that the asymptotic solution by the approximate method is $\sqrt{3}/2$ times the correct value. This disagreement is not unexpected in view of the fact that the approximate solution is based on the assumption that σ_n is small, and in fact this difference as $\sigma_n \longrightarrow \infty$ is surprisingly small. Although the approximate solution agrees quite well with the exact solution for the specific geometry used here, care should be taken in employing this type of linearization method for other geometries. For example, a rapid deviation from the exact solution occurred when the same

approximate method was tried on a system of a cylindrical porous catalyst [14].

Note that all of the above analysis can be applied, only with appropriate changes in the sign of the concentration gradient, to a system where diffusion occurs toward the center of a circle, since we have not assumed $\eta_o > 1$ in any part of the development except for the sign of the concentration gradient for Eq. (11).

NUMERICAL EXAMPLE

It is of interest to perform an order-of-magnitude numerical calculation applying the preceding analysis to a set of parameters characteristic of a real catalyst. The region of interest for such a calculation is near the value of the surface-diffusion modulus $\hat{\sigma}_n$ where the effectiveness factor $\mathcal{E}$ starts falling off from unity. This region is where the effects of diffusion and of kinetics are of comparable magnitudes.

For lack of consistent data on kinetics and diffusion for a particular real system, reasonable values of kinetic parameters will be assumed and surface diffusivities which correspond to the region of interest will be calculated.

Suppose, for an order-of-magnitude calculation, that the rate constant is given by the following simple expression of transition state theory:

$$k_n \cong \left(\frac{kT}{h}\right) e^{-E_r/RT} \tag{22}$$

where k is the Boltzmann constant and h the Planck constant. At 300°K,

$$k_n \approx 10^5 \quad \text{for } E_r = 10{,}000 \text{ cal/mol}$$
$$\approx 10^2 \quad \text{for } E_r = 15{,}000 \text{ cal/mol}$$
$$\approx 10^{-2} \quad \text{for } E_r = 20{,}000 \text{ cal/mol}$$

A typical reforming catalyst would consist of about 1% platinum impregnated on alumina with specific area of about 100 m^2/g. The diameter of the platinum center is of the order of 100 Å. Assuming the platinum center to be hemispherical in shape, the ratio of the distance between the centers to their diameter, i.e. η_o, becomes about 20.

The value of $\hat{\sigma}_n$ where ε starts falling off from unity for $\eta_o = 20$ is about 3×10^{-2}, from Fig. 2.

Assuming a first-order reaction, the corresponding surface diffusivities at 300°K from the definition of $\hat{\sigma}_n$ become:

$$D_s \approx 10^{-5} \text{ cm}^2/\text{sec} \quad \text{for} \quad k_1 \approx 10^5 \text{ sec}^{-1}$$
$$\approx 10^{-8} \text{ cm}^2/\text{sec} \quad \text{for} \quad k_1 \approx 10^2 \text{ sec}^{-1}$$
$$\approx 10^{-12} \text{ cm}^2/\text{sec} \quad \text{for} \quad k_1 \approx 10^{-2} \text{ sec}^{-1}$$

From these values it is not unreasonable to expect marked diffusional effects in real catalytic systems considering the range of observed values of surface diffusivity of chemisorbed species at 300°K. Gomer and associates [6,7,8] obtained surface-diffusivity values ranging from 4×10^{-3} cm^3/sec for O_2 on W [7] to 4×10^{-10} cm^2/sec for H on W [8], and to 3×10^{-20} for O_2 on W [7]. Robell et al. [11] observed a surface diffusivity of 3.4×10^{-19} cm^2/sec for hydrogen on carbon.

For a system of a given reaction-rate constant and surface diffusivity, $\hat{\sigma}_n$ can be varied several orders of

magnitude by changing the temperature and/or R_i to obtain a desired value of the effectiveness factor.

The above order-of-magnitude calculation shows that for a real catalyst a situation can exist where the net rate of a surface reaction is influenced by both intrinsic kinetics and surface diffusion.

The results are also applicable to a catalytic surface which has only a limited number of discrete adsorption sites, but with the rest of the surface kinetically active to adsorbed species. In this case the parameter η_o has a slightly different meaning than for a supported metal. If R_i is the order of atomic dimensions then $(\eta_o)^2$ is just the reciprocal of the ratio of the number of active adsorption sites to the total number of surface sites. These calculations, then, apply to a range of fractional coverages of active sites from 0.0001 to 0.25 and could be applied to reactions on surfaces so characterized. The results of the numerical calculation mentioned above (active coverage of 0.0025) and the reported values of surface diffusivities indicate that many single-component catalytic surfaces which are heterogeneous relative to adsorption may also be strongly influenced by surface diffusion.

The extension of this model to interpret catalytic effects of mechanical mixtures and isomorphically substituted mixtures is not yet complete. Preliminary calculations indicate that both types of mixtures have large effectiveness provided a bulk diffusion mechanism is operating.

NOTATION

C	surface concentration
D_s	surface diffusivity
E	activation energy
$\mathcal{E}$	effectiveness factor
I_j, K_j	modified Bessel function of the first and second kinds, respectively, with the subscripts designating the order
k_n	nth order intrinsic surface-reaction rate constant
n	intrinsic reaction order
R	gas constant
R_i	radius of the adsorption center or the island
R_o	one-half the distance between the adsorption centers
r	radial coordinate
T	temperature
v	rate of reaction per unit area of the adsorption center as defined in Eq. (12)

Greek Letters

η	dimensionless radial coordinate
η_o	R_o/R_i

σ_n surface-diffusion modulus for nth-order surface reaction as defined in Eq. (4)

$\hat{\sigma}_n$ generalized surface-diffusion modulus for nth-order surface reaction

ψ dimensionless surface concentration

$\Delta\psi$ perturbation term of ψ [see Eq. (17)]

Subscripts

d for surface diffusion

n parameter for n-th order reaction

r for intrinsic surface reaction

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APPENDICES

APPENDIX A

SPECIFICATIONS OF "AS RECEIVED" AMMONIUM PERCHLORATE

The following specifications were reported by the manufacturers for the three sources of ammonium perchlorate used in this study:

(1) Pennsalt Chemical Corporation (P):

Reagent grade

Minimum ammonium perchlorate	99.5%

Maximum impurities specified were:

Chlorates as NH_4ClO_3	0.01
Chlorides as NH_4Cl	0.10
Bromates as NH_4BrO_3	0.001
Water insoluble	0.00
Sulfates as $(NH_4)_2SO_4$	0.00
Non-alkali metals as oxides	0.00
Sodium and potassium	0.05%

(2) Matheson, Coleman and Bell (M)

Reagent grade

Maximum impurities specified were:

Chloride and chlorate (as Cl)	0.01%
Calcium (Ca)	0.010
Heavy metals (as Pb)	0.001
Insoluble matter	0.010
Iron (Fe)	0.001
Sodium (Na)	0.03
Sulfate (SO_4)	0.005%

It was observed that ammonium perchlorate from this source contained some black particles of an unknown impurity which was insoluble in water.

(3) American Potash and Chemical Corporation (A):

Minimum ammonium perchlorate 99.5%

No detailed specification of impurities was available.

APPENDIX B

EXPERIMENTAL DATA

Tables B-1 and B-2 present the data on the deflagration rate of ammonium perchlorate at 1000 psig and 3500 psig respectively. The accuracy of densities reported is ± 0.01 g/cm^3. In Table B-1, the sixth and seventh columns show the results of two different photographic analyses of the same pellet along two different lines. The arithmetic average of these two results is shown in the eighth column. In all three tables of this appendix the last column shows the corrected burning rate at 21°C. For this correction, the change in burning rate with temperature is considered to be one percent per degree centigrate at 1000 psig and two percent per degree centigrade at 3500 psig. The second column in these tables shows the source of ammonium perchlorate and the degree of recrystallization. The abbreviations "P", "M" and "A" stand for Pennsalt, Matheson and American Potash. The numbers following these letters show the degree of recrystallization (number of times the ammonium perchlorate is successively recrystallized).

Table B-1

Deflagration Rate of Ammonium Perchlorate Pellets at 1000 psig

Run No.	Type	Length cm	Density g/cm^3	Ambient temp °C	Deflagration rate at ambient temp. (First analysis) cm/sec	Deflagration rate at ambient temp. (Second analysis) cm/sec	Average Deflagration rate at ambient temp. cm/sec	Deflagration rate at 21°C cm/sec
483	P1	1.83	1.94	19	0.85	0.76	0.80	0.82
484	P1	1.78	1.94	21	0.87	0.89	0.88	0.88
485	P3	1.64	1.94	21	0.72	0.71	0.71	0.71
486	P4	1.77	1.95	21	0.76	0.72	0.74	0.74
487	P4	1.70	1.94	22	0.77	0.81	0.79	0.78
488	M1	1.68	1.94	20	0.87	a	0.87	0.88
490	M1	1.67	1.94	22	1.00	a	1.00	0.99
491	M4	1.87	1.94	21	0.80	0.76	0.78	0.78
493	M2	1.73	1.95	21	0.84	0.87	0.85	0.85
513	M4	1.70	1.95	23	0.80	0.84	0.82	0.80
514	A1	1.84	1.94	23	0.74	0.73	0.73	0.71
515	A3	1.65	1.94	23	0.90	0.91	0.90	0.88
516	M0	1.68	1.94	23	0.93	0.96	0.94	0.92
517	M0	1.86	1.94	22	0.93	0.95	0.94	0.93
518	A3	2.07	1.94	22	0.73	0.71	0.72	0.71
520	M3	1.75	1.93	23	0.76	a	0.76	0.74
489	A2	1.72	1.95	22	0.88	a	0.88	0.87
522	A0	2.10	1.94	27	0.94	0.96	0.95	0.89
523	A0	2.09	1.94	27	0.94	0.91	0.92	0.86
524	P0	2.28	1.93	26	0.98	1.02	1.00	0.95
525	P0	2.08	1.92	26	0.99	0.99	0.99	0.94
526	A1	1.76	1.95	23	0.87	a	0.87	0.85
527	M3	1.95	1.95	23	0.89	a	0.89	0.87
528	A4	1.77	1.95	22	0.85	a	0.85	0.84
529	A4	1.93	1.95	22	0.81	a	0.81	0.80
560	P3	2.24	1.94	21	0.76	a	0.76	0.76
561	P2	1.86	1.94	21	0.86	a	0.86	0.86
562	M2	1.69	1.94	20	0.84	a	0.84	0.85
563	A2	1.67	1.94	20	0.84	a	0.84	0.85
564	P4	2.20	1.94	20	0.74	a	0.74	0.75
565	P2	2.11	1.94	20	0.71	a	0.71	0.72

[a] The second photographic analysis was not necessary because of the uniform propagation of the burning surface.

Table B-2. Deflagration Rate of Ammonium Perchlorate Pellets at 3500 psig

Run No.	Type	Length cm	Density g/cm^3	Ambient temp. °C	Deflagration rate at ambient temp. cm/sec	Deflagration rate at 21°C cm/sec
626	P0	1.70	1.94	20	0.75	0.76
627	P0	1.92	1.94	21	0.72	0.72
628	M0	1.95	1.93	21	0.78	0.78
629	P1	2.03	1.94	20	1.23	1.25
630	P1	2.00	1.95	20	1.31	1.33
631	M1	1.81	1.94	20	0.44	0.45
632	M1	1.94	1.94	20	0.30	0.31
633	M2	1.92	1.94	20	1.21	1.23
634	M2	1.90	1.94	20	1.31	1.33
635	M3	1.90	1.94	20	1.16	1.18
636	P3	1.87	1.94	20	1.23	1.25
638	M4	1.86	1.94	21	1.15	1.15
639	P3	1.83	1.93	21	1.26	1.26
640	M4	1.89	1.93	21	1.23	1.23
641	M0	1.89	1.93	21	0.98	0.98
642	P4	1.86	1.94	21	1.26	1.26
643	P2	1.88	1.94	21	1.13	1.13
644	P2	1.88	1.94	21	1.30	1.30

Table B-3

Deflagration Rate of Pellets of Undried Ammonium Perchlorate at 1000 psig

Run No.	Type	Length cm.	Ambient temp. °C	Deflagration rate at ambient temp. cm/sec	Deflagration rate at 21°C cm/sec
445	P1	1.58	21	0.97	0.97
446	P1	1.72	22	1.12	1.11
447	P1	2.10	20	0.93	0.94
448	P1	2.01	22	0.97	0.96
339	P1	1.73	21	1.11	1.11